THE CORROSION RESISTANCE OF TIN AND TIN ALLOYS

S. C. BRITTON, M.A.

TIN RESEARCH INSTITUTE

Three Shillings and Sixpence

The Tin Research Institute is financed by Tin Producers in the Belgian Congo, Bolivia, Indo-China, Indonesia, Malaya and Nigeria. The Institute is controlled by the International Tin Research and Development Council, which consists of delegates from these six Tin producing countries, the Council being presided over by an independent Chairman.

The researches of the Institute are directed to develop the use of Tin and are based on scientific study of the metal, its alloys and compounds and of industrial processes which use Tin or may provide future markets.

The library contains a wide range of up-to-date information, and technical experts are available for consultation and practical assistance, either in the laboratories or at users' works.

Enquiries are welcomed at the address shown below and no charge is made for information or assistance.

Headquarters and Laboratories:

Great Britain

Tin Research Institute,
Fraser Road, Greenford,
Middlesex.

Technical Representation in:

Belgium and France

Centre d'Information de l'Etain,
31 Rue du Marais,
Brussels,
Belgium.

Holland

Technisch Informatie Centrum
voor Nederland,
Louis Couperusplein 19,
The Hague.

United States of America

Tin Research Institute, Inc.,
492 West Sixth Avenue,
Columbus, 1,
Ohio.

	Date	Date	

TLm

THE CORROSION RESISTANCE OF TIN AND TIN ALLOYS

S. C. BRITTON, M.A.
Head of Corrosion Department,
Tin Research Institute.

Published by
TIN RESEARCH INSTITUTE
FRASER ROAD, GREENFORD, MIDDLESEX
APRIL, 1952

Preface

The corrosion resistance of tin has been recognised from the earliest times. Ancient writings and archaeological discoveries reveal a long history of use as an ornamental material and as a coating for other materials. Tin, in addition to silver and gold, adorned the shield of Achilles. In Pope's translation of the Iliad (Book 18) we have in the description of its production:

In hissing flames huge silver bars are rolled
And stubborn Brass and Tin and solid Gold.

and

A darker metal mixed intrenched the place
And pales of glittering Tin the enclosure grace.

The 'brass' and the 'darker metal' were no doubt what is now termed bronze, a copper-tin alloy which also has a long history of use and ornament. In addition a copper-tin alloy with good reflecting and tarnish-resisting qualities formed the mirrors of the ancient world.

Tin and its alloys have continued to find ever-increasing uses; for most of these, corrosion resistance is important and, for many, it is the reason for their use. In this publication an attempt has been made to present the essential features of the corrosion resistance in a convenient form.

Defences against corrosion, or against other ills, are seldom proof against all attacks. In order to prepare defence, it is very desirable to know the nature of the attack expected and inevitably much of this publication deals with the occurrence of corrosion. It should be understood that some of the instances of corrosion mentioned may in practice occur only occasionally since restraining influences which, for clarity of exposition, may be mentioned separately, are often provided in service conditions.

In dealing with corrosion, it is rarely possible to quote precise measurements of loss of weight or of strength which can immediately be used to assess the life of a metal in service. Temperature, aeration, the concentration of the corroding agent and the presence of other substances may all produce important changes so that experimental measurements, usually made under simple conditions, seldom reproduce a service environment. Given however some guiding principles, backed by results obtained in defined conditions, it is usually possible to diagnose the cause of an instance of corrosion and to assess the prospects of a metal in new circumstances. The object of this publication is to provide this guidance for tin and its alloys. In order to keep it within a convenient length, some important matters are only briefly summarised, but more details may be sought in the literature cited.

Inevitably, owing to the wide application of tin and its alloys, and the rapidity of changes in some fields, there will be gaps, especially in the infor-

mation concerning practice, and some information may be out-of-date by the time this is read. It is hoped that readers will not hesitate to draw the attention of the Tin Research Institute to matters which they feel are inadequately dealt with, so that the practical usefulness of this publication may be improved.

S. C. B.

August, 1951

Contents

Introduction

The metal tin is mechanically weak, and although it has, pure or only lightly alloyed, some applications as tubing, collapsible tubes and foil, its main uses are as a protective coating for stronger materials and as an alloying element. All uses are considered in the publication, which is arranged in three parts: I. Tin; II Alloys of Tin; and III. Coatings of Tin and Tin Alloys. The division between the content of the parts is not, however, sharp, for much of Parts I and II applies to tin and its alloys used either as continuous coatings or as solid metal. The coatings dealt with in Part III are those of alloys which have their main use as coatings and those of other alloys and of tin whose performance cannot be divorced from effects of the basis metal exposed at their discontinuities.

For the understanding of all parts, some knowledge of the basic corrosion processes and of the relation of the properties of tin to them, is helpful. This can be gained from one of the several books dealing generally with corrosion, but a brief outline may be given here for the benefit of those who require only essentials.

Corrosion of metals by aqueous media is an electrochemical process accompanied by the flow of current between areas of the surface where metal passes into solution, usually termed 'anodes', and other, uncorroded, areas where hydrogen is discharged as a gas or oxidised, usually termed 'cathodes'. The two types of area may be large and spaced apart or very tiny and side by side. When two metals are joined together, one may act wholly as cathode and the other as anode, although both may have areas of the two types. Heterogeneity of the metal surface or in its environment may produce the two types of area on one metal, whether or not a second metal is present. The process resembles that familiar in primary batteries in which the positive pole, usually carbon or copper, behaves like the cathode of the corrosion cell and the negative pole, usually zinc, corresponds to the anode. The performance of corrosion cells is subject to the same considerations of polarisation and internal resistance that affect batteries.

The rate of solution of the metal is governed by the size of the corrosion currents. This may be influenced by the magnitude of the potential difference produced by the heterogeneity concerned, by the polarisation characteristics of the anodes and cathodes, by the electrical resistance of the corroding medium and by the formation of obstructive layers on the surface. (Obstructive layers may be present initially (see below) or may be formed by the production of an insoluble compound at the anodes or by secondary products formed by the interaction of the products first formed at anodes and cathodes

with one another or with other materials present.) The corrosion current is often determined by only one of its possible modifiers, since the whole corrosion process can only go as fast as its most sluggish part. For instance, if the cathode areas become severely polarised, current flow, and hence the rate of corrosion, may become limited by the rate of supply of a depolarising agent.

An important feature of the performance of the cathode areas is the facility with which hydrogen can be evolved as gas from them. This property for each metal is indicated by the 'hydrogen overpotential'. If this is high, hydrogen gas is only evolved with difficulty and current flow will consequently be restricted unless oxygen or some other oxidising agent is available to remove hydrogen by oxidation.

The metal may initially have on it an obstructive film, formed by combination of its surface layer with atmospheric oxygen. The subsequent value of this film, which is usually too thin to be visible, depends on the corroding agent. In some environments it may be quickly dissolved, but in others it may be a good foundation for the formation of a more robust protective layer by the precipitation of insoluble compounds at any weak points in it where corrosion makes a start.

When two metals are corroding in contact with one another, some idea of which is likely to be predominantly cathodic or more 'noble' is given by their relative positions in the 'Electrochemical Series'. This is a list of the normal electrode potentials of the metals, i.e. of their potentials relative to hydrogen when immersed in solutions of their own salts of 'normal' concentration. This is, however, a rather uncertain guide even to the direction of current flow in all conditions and even less reliable as an indication of whether one of the two metals of a couple will have its corrosion stimulated by contact with the other. The different polarisation characteristics of the two metals may considerably modify and even reverse the current flow after brief corrosion. Moreover, in the case of one metal exposed at pores in a coating of another, the electrical resistance of the pore channels may exercise an important influence which is affected both by the thickness of the coating, which dictates the length and often the diameter of the channel, and by the formation of plugs of corrosion product in the channel.

The relation of the properties of tin and its compounds to these considerations may now be examined.

A clean, dry tin surface exposed to air carries a thin invisible oxide film. In near-neutral environments this is stable and protective, providing a good foundation in neutral media for the sealing by precipitated product of any weak spots in it where corrosion is initiated. The film is, however, soluble in both acids and alkalis and therefore does not normally contribute to the protection of the metal against such media.

Many of the simple salts of tin are freely soluble in water so that they do not produce obstructive layers but the chromate, phosphate, borate and silicate are capable of giving insoluble products and, in addition, oxides and basic salts may be precipitated on the surface in some conditions.

The hydrogen overpotential of tin is one of the highest, 0·85 volts for a current density of 0·001 amps. per sq. cm. This has the effect that, in a wide variety of conditions, hydrogen gas is not evolved from tin so that the rate of corrosion becomes controlled by the supply of oxygen or other oxidising agents and in their absence is negligible.

The normal electrode potential of tin with reference to hydrogen is —0·136 volts at 25° C., i.e. in the 'Electrochemical Series' it appears as likely to be cathodic to iron, cadmium or nickel but anodic to copper. This is, however, a very uncertain guide to the corrosion of tin when coupled to other metals. In some organic acids, including those present in fruit juices, the polarity between tin and iron is reversed, so that tin becomes the predominantly anodic member of the couple. Tin coatings on steel may therefore act in two ways as is exemplified by the inner and outer surfaces of the fruit can. Inside the can, the tin coating is anodic and suffers some corrosion but gives protection to any steel exposed. On the outer surface, exposed to the air, the tin coating is usually cathodic to steel and is not itself corroded. This, fortunately, is to the advantage of both surfaces for, inside, the corrosion of unprotected steel might be sufficiently rapid to perforate the can but outside, in normal storage conditions, rusting of the steel is slow enough to need no restriction by sacrificial corrosion of the coating which remains bright and attractive.

In tin alloys, the electrode characteristics of tin are modified by the presence of the other metals, but instances will be mentioned in the following pages of the contribution of tin to the formation on alloys of stable oxide films in air and of oxide or basic salt layers in solution.

Part I
CORROSION OF TIN

ATMOSPHERIC CORROSION

The surface of dry tin is normally covered by an oxide film and quickly regains it on exposure to air if it is destroyed by reduction, solution or abrasion. A film isolated by solution of the metal in ferric chloride gave stannic reactions.[1] The stannic oxide lattice is cation rich, a character which is expected to produce resistance to film thickening and tarnishing.[2 3] The film does in fact thicken only very slowly when the metal is heated and begins to show interference colours only at about 200° C. Tin melts at 232° C. so that its resistance to oxidation when heated has not a wide application. One use is that of tin wire for electrical fuses. Here the resistance of the metal to oxidation on heating and to corrosion by indoor atmospheres at ordinary temperatures ensures stability in performance over long periods and prevents the formation of a skin such as may, on some metals, delay rupture after fusion.[7]

When tin is exposed to sheltered indoor conditions, it remains bright almost indefinitely. Measurements of reflectivity[4] indicated a very slight decline and showed that, if the metal was cleaned every three weeks, a water wash restored the metal to its starting condition after three and six weeks' exposure: thereafter a soap and water wash was required, but this sufficed for the twenty-six weeks' duration of the experiment to keep the reflectivity nearly unchanged.

Measurements of weight change[5] showed that indoors, tin was less corroded than copper, zinc, or cadmium. The corrosion of tin was trifling but, persistent, the weight increment increasing in proportion to the time of exposure.

In a Stevenson screen, with full out-of-door humidity changes but no rain, tin was slightly inferior to copper but superior to nickel. Here the character of the corrosion product came into play and the deliquescent products forming on nickel were harmful to it, whereas the stable basic compounds on copper tended to be protective. The product on tin may be regarded as neutral. In full exposure to the weather at Birmingham, tin and its alloys were superior to nickel, copper, brass, zinc, and cadmium in that order. Some results are shown in Table I.

American exposure tests at a variety of locations over a period of ten years confirm that the good resistance of tin is maintained, although marine exposures caused rather more rapid corrosion than industrial and rural atmospheres. Some of the results are shown in Table II.[6]

TABLE I

OUTDOOR LOSS IN WEIGHT TESTS OF ONE YEAR'S DURATION

Material	Loss in weight after removal of Corrosion product (Mg./sq. dm.)
Pure Tin (99·98%) ..	111
Antimonial Tin (2·2% Sb)	112
Cupriferous Tin (0·2% Cu)	127
Nickel	306
H.C. Copper	314
70/30 Brass	345
Zinc	380
Cadmium ..	879

TABLE II

A.S.T.M. TESTS ON ATMOSPHERIC CORROSION OF TEN YEARS' DURATION

Exposure site	*Atmosphere*	*Average Penetration (in. × 10⁻⁴)*					
		Tin	*Copper*	*Lead*	*Lead*	*Nickel*	*Aluminium*
Altoona, Pa.	Severe Industrial	6·03	4·64	2·67	19·10	15·15	2·44
New York	Severe Industrial +Marine	4·71	4·71	1·67	19·32	12·81	3·15
Key West Fla.	Marine	8·41	1·98	2·16	2·05	0·47	0·36
La Jolla, Calif.	Marine	9·05	5·21	1·62	6·85	0·43	2·81
State College Pa.	Rural	1·75	2·28	1·88	4·20	0·61	0·12
Phoenix Ariz.	Rural (dry)	1·28	0·53	0·94	0·99	0·12	0·01

These long-term tests are rather of academic interest, for tin is unsuited in strength (and in price) to use unalloyed for any purpose involving full exposure to the weather. What is important is the retention of brightness or semi-brightness for a long period in sheltered conditions. The almost indefinite retention of brightness by tin in indoor conditions enables collapsible tin-tubes, tin-foil wrappings and tin-coated steel to provide attractive packages. Some use of tin has been made in the production of costume jewellery from the earliest historic times and still persists.

Pollution of air with sulphur dioxide and hydrogen sulphide, the agents usually responsible for tarnishing and corroding metals, has little effect on tin. Very strong sulphur dioxide pollution, in excess of that in the most grossly polluted industrial atmospheres, causes tarnishing and even darkening, the sulphur dioxide being reduced to produce a sulphide film. Hydrogen sulphide is likely to have some action at temperatures above 100° C.

Tin is attacked by halogens and by vapours of their acids and is therefore etched when above strong solution of these materials. Fluorine is not however active at ordinary temperatures but becomes corrosive above 100° C.

The vapour from glacial acetic acid corrodes tin but the vapours from weak solutions of the acid, e.g. from vinegar or from wood, have no effect. Tin is also unaffected by the vapours of organic acids which when evolved from some insulating materials frequently cause corrosion of cadmium and zinc in electrical equipment.

The mutual effects of tin and other metals in contact with one another under atmospheric corrosion was studied by exposure of couples in the form of discs in a variety of American localities.[8] The results do not necessarily indicate what happens at pores in a tin coating (see p. 46), but give some guidance as to what may happen when tin or tin coated material is exposed in contact with a large surface of another metal.

In marine environments, the corrosion of tin was stimulated by contact with copper and iron, retarded by contact with zinc and aluminium and unaffected by contact with lead and nickel, although in a severe marine exposure, nickel accelerated corrosion. In industrial areas, acceleration was produced by contact with copper and slightly by contact with iron, retardation was produced by contact with nickel, aluminium and zinc and there was no effect with lead. There was some tendency for contact with tin to make iron corrode less in marine environments and more in industrial areas.

REFERENCES

1. Kutzelnigg, A., Zeitsch. Anorg. Chem. (1931) **202**, 418.
2. v. Baumach, H. H. and Wagner, C., Zeitsch. Physikal. Chem. (1933) B, **22**, 199.
3. Price, L. E. and Thomas, G. J., J. Inst. Met. (1938) **43**, 357.
4. Kenworthy, L. and Waldram, J. M., J. Inst. Met. (1934) **55**, 247.
5. Kenworthy, L. Trans. Faraday Soc. (1935) **31**, 1331.

6. Finkeldey, W. H., Rep. of Sub-Comm. VI. Proc. A.S.T.M. (1943) **43**, (1) 137.
7. Nicholson, G. W., Elect. Rev. (1937) **120**, 500.
8. Reports of Sub-committee VIII on Galvanic and Electrolytic Corrosion, Proc. A.S.T.M. (1935) **35** (1), 167; (1939) **39** (1), 296.

CORROSION BY ACIDS

In the presence of air, tin suffers some corrosion by mineral acids and by many organic acids. In general the corrosion is slow in the absence of air because of the reluctance of the metal to liberate hydrogen, but is increased by a supply of oxygen, from the air or from an oxidising agent, to act as a depolariser (see Table III). It is also increased by influences which improve the chances of hydrogen evolution, e.g. rise in temperature and rise in the concentration of acid (see Table IV). Oxidising acids such as nitric are corrosive, and the addition of oxidising agents to any acid is likely to cause increase of attack, but in some circumstances a sufficient addition of an oxidising agent can produce passivity, e.g. chromic acid added to sulphuric and phosphoric acids or hydrogen peroxide added to citric acid in sufficient amounts have been shown to stop corrosion.

The effect of limitation in oxygen supply on the action of mineral acids is illustrated by the results quoted in Table III.[1]

TABLE III

CORROSION OF TIN BY ACIDS IN PRESENCE AND ABSENCE OF OXYGEN

Acid	*Weight loss (mg. per sq. dm. per day)*	
	Under Hydrogen	*Under Oxygen*
3% Nitric	630	640
6% Hydrochloric	60	11,100
6% Sulphuric	35	4,300
6% Acetic	15	2,300

The effect of concentration of acid in the absence of air is illustrated by the results quoted in Table IV.[2]

Attack by mineral acids is too great to permit the use of tin or tin coatings in handling them, but it is sometimes necessary to clean, with acids, tinned equipment used for other purposes, e.g. to remove a scale deposited from

water or milk. From what has been said it follows that, in such a use, nitric acid should be avoided and the weakest acid consistent with effective cleaning should be used, in quiescent conditions. The organic inhibitors used to inhibit the attack of steel by acids during pickling are rather ineffective on tin, but the addition of stannous chloride to hydrochloric acid of below 1 per cent. strength has a pronounced restraining action, at least in the absence of aeration. An addition of 10 p.p.m. stannous ions reduced the corrosion by 0·1 per cent. HCl from 7·2 mg./sq. dm./day, itself a small figure, to 1·6, an almost negligible one.[2]. Phosphoric acid has much less action than other mineral acids (see Table V) and is therefore a safer cleaning agent for tin, although organic acids may be better (see p. 19).

TABLE IV

CORROSION OF TIN IN AIR-FREE ACIDS

Concentration per cent.	*Duration of experiment (hours)*	*Weight loss, calculated as mg. per/sq. dm.per /day*	
		Sulphuric	*Hydrochloric*
20	1	290	190
10	1	36	72
5	1	48	36
1	1	24	36
1	10	10·8	6
0·5	10	14·4	10·8
0·1	10	13·2	7·2
0·05	10	8·4	14·4

Corrosion by organic acids is normally slower than it is for mineral acids and the effect of restricted oxygen supply is more marked since the lower hydrogen ion activity makes the evolution of hydrogen more difficult. Comparative figures for weight losses of tin fully immersed in 0·1 N acids without exclusion of air are presented in Table V.[3] The figure included for oxalic acid is a gain in weight due to adherent corrosion product: this acid is, however, one of the more corrosive organic acids. The comparatively slow action of phosphoric acid in these conditions is noteworthy.

In the absence of oxygen or oxidising agents from the solution or from the gas above it, corrosion of tin was barely detectable after 28 days' immersion in citric acid/sodium citrate solutions with pH values of 2·4–5·5[4]. In the presence of air, corrosion took place without much effect of the pH value within the range studied and oxidising agents in the solution, e.g. ferric citrate, promoted corrosion even when no air was present.

Tin forms complex ions with some organic acids, notably citric and oxalic. The depletion of the solution in tin ions thereby caused has the effect of depressing the electrode potential of tin to an extent which makes the metal

anodic to steel.[5] The reversal of polarity had been known to occur long before the explanation of complex ion formation was advanced.[6 7 8] It is of very great importance for the handling of fruits in tin-coated steel since anodic corrosion of the tin gives protection to steel exposed at discontinuities in the coating. This matter will be considered further in Part III (p. 50). Meanwhile it should be borne in mind that some of the results quoted in this section for the corrosion of tin may be an uncertain guide to the suitability of tin-plate for handling a product, since a slight corrosion of a tin coating may be tolerated when the underlying metal is thereby protected.

TABLE V

CORROSION OF TIN (3×1 IN.) FULLY IMMERSED IN 0·1 N SOLUTIONS OF ACIDS AT 25° C. FOR SEVEN DAYS

Acid	*pH of solution*	*Loss in weight (g.)*
Tartaric	2·14	0·020
Lactic	2·23	0·029
Citric	2·32	0·028
Malic	2·41	0·022
Succinic	2·73	nil
Acetic	2·88	nil
Oxalic	1·46	0·058*
Hydrochloric	1·05	0·042
Sulphuric	1·16	0·019
Phosphoric	1·71	0·002

* Weight gain

TABLE VI

CORROSION OF TIN FULLY IMMERSED IN ACETIC ACID IN PRESENCE OF AIR

Concentration per cent.	*Temperature*	*Corrosion Rate as penetration (in. per month)*
20	25° C.	0·000412
	Boiling	0·000896
60	25° C.	0·000511
	Boiling	0·00131
100	25° C.	0·00160
	Boiling	0·0140

Cold dilute solutions of acetic acid are not corrosive to tin (see Table V), but, when hot or strong, the acid is rather corrosive to tin either immersed in it or in its vapour. The weak concentration of the acid above vinegar is not however very corrosive, and tin capsules can be used in closures to vinegar bottles. Results[9] shown in Table VI give some indication of the effects of concentration and temperature. (See also Table V for comparison with other acids in dilute solution.)

Oleic and stearic acids are not corrosive at room temperatures and tin tubes can be used to contain cosmetic materials, etc., based on them. At temperatures of 330°–340° C. stearic acid was found to be corrosive.[10]

Phenol was found[13] to have no effect after contact with tin for 18 months at 30° C., but above 100° C. some reaction quickly occurred.

The weaker organic acids have usually a negligible action and their use in solutions incorporating organic detergents has been recommended for the cleaning of dairy vessels. For this purpose, their acidity is sufficiently high to prevent scale deposition on the metal, but is low enough to avoid corrosion. Gluconic acid has been used commercially and levulinic and hydroxy-acetic acids have been mentioned as possibilities. Insufficient information is, however, available to say how such agents compare in performance and cost with other cleaning agents.

Carbonic acid has only a very slight action and carbonated beverages are safely handled in tin or in tinned metal, although if their acidity is raised by flavouring substances, some wastage of metal must be expected. Beer causes a trifling loss of metal, but this can induce a haze, apparently by the reaction of the trace of tin dissolved with proteins. The action is usually stopped by the formation of an obstructive layer on the tin after a period of use, and there has been an extensive use of block tin pipes for conveyance of beer from cellar to bar. This use is now somewhat diminished as mechanically stronger corrosion-resistant materials have become available, but it has some advantages in providing pipes easy to manipulate and to join.

Much attention was given some years ago, especially in Germany, to the haze produced by tin, since the effect seemed not insuperable and was not as bad as the effect produced by some of the other materials available for piping and for brewery equipment. It was found that the character of the beer was important, the degree of hazing increasing with acidity and being relatively slight when waters high in carbonate were used for brewing and relatively bad for high sulphate waters.[11]

Although these findings help to explain why experience of haze production varies between users, beer cannot be changed to suit its containers. The important prevention measure appears to be to develop a protective layer on the metal by a period of use and then to guard, by careful cleaning, against its destruction. The pretreatment with beer residues of tinned copper equipment used in the brewery has been recommended,[12] this being carried on until the tin acquires a yellow colour.

In the packing of beer in tinplate containers, the formation of a protective

layer would of course avail little, since the initial action would leave permanent effects. Moreover, small quantities of iron such as might be derived from the pores in the coating have an adverse effect on flavour. Special lacquers are therefore used to coat such containers.

REFERENCES

1. Whitman, W. G. and Russell, R. P., Ind. Eng. Chem. (1925) **17**, 348.
2. Kohman, E. F. and Sanborn, N. H., Ind. Eng. Chem. (1928) **20**, 1373.
3. Bryan, J. M., Ann. Rep. Food Investigation Board, D.S.I.R. (1936), p. 185.
4. Bryan, J. M., Trans. Faraday Soc. (1931) **127**, 606.
5. Hoar, T. P., Trans. Faraday Soc. (1934) **30**, 472.
6. Mantell, C. E. and King, W. G., Trans. Amer. Electrochem. Soc. (1927) **52**, 435.
7. Kohman, E. F. and Sanborn, N. H., Ind. Eng. Chem. (1928) **20**, 76.
8. Lueck, R. H. and Blair, H. T., Trans. Amer. Electrochem Soc. (1928) **54**, 257.
9. Calcott, W. S. and Whetzell, J. C., Trans. Amer. Inst. Chem. Eng. (1923) **15**, 1 and 142.
10. Kino, K., J. Soc. Chem. Ind. (Japan) (1937) **40**, 312B.
11. Schonfeld, F. and Hirt, W., Woch. Brau. (1910) **27**, 633.
12. Seyffert, H., Woch. Brau. (1904) **21**, 398.
13. Zoller, H. F., J. Am. Chem. Soc. (1921) **43**, 211.

CORROSION BY ALKALIS

Tin is corroded by alkalis if the pH be sufficiently high to dissolve the oxide film on the metal. The actual pH value at which this occurs depends on the temperature, the state of the film and the composition of the solution. Potential measurements, made in solutions of sodium carbonate and bicarbonate, with pure tin carrying an oxide film formed at room temperature after abrasion with emery, indicated activity at pH values down to 8·4; but if the film were thickened by heating the metal in air at 210° C., it was not removed by solutions with pH value 11·2.[9] The author has found as-rolled surfaces to remain passive in solutions with pH values up to 11 at 20° C., but to become corroded at 40° C.

The presence of halide ions appears to increase the pH necessary for activity. The addition of 0·06 per cent. of sodium chloride to carbonate solutions, active at pH values above 8·4, raised the threshold pH for activity above 9·5.[10] Additions of silicate, phosphate, copper, silver, lead or zinc ions also favoured passivity, but sulphide ions promoted activity.[11] It is thus difficult to predict a limiting pH value for any complex product, but many materials with pH below 11, such as the less alkaline solutions of sodium

phosphate and sodium silicate, are without effect at ordinary temperatures.

In addition to their effect in raising the minimum pH for corrosion to occur, some anions have an effect on the rate of corrosion in solutions with pH values above the limit, no doubt owing to the production of obstructive layers on the metal surface. Thus, when the corrosion rate is not controlled by some factor other than the composition of the solution, phosphate and silicate solutions are rather less active than solutions of caustic soda or soda ash of equivalent alkalinity. However, the most important practical aspect of corrosion by alkalis arises from the use of alkaline detergents for cleaning tinned ware. In this field, the choice of the nature and concentration of the alkali is normally based on the primary function of cleaning. Moreover, as explained below, the amount of corrosion may be controlled by some factor other than the composition of the solution, such as the aeration of the liquid. It is therefore difficult to recommend any alkaline material for detergent use solely on the basis of corrosion.

When the pH value to initiate corrosion is exceeded, the progress of attack is governed by considerations similar to those applying to corrosion by acids, i.e. since the high overpotential restricts evolution of hydrogen, the corrosion rate depends on the supply of oxygen or other depolarising agent to the metal surface.

The removal of dissolved oxygen by addition of sodium sulphite can make alkaline solutions almost non-corrosive to tin.[1] A practical recommendation is that one part in four of sulphite be added to caustic soda or one part in ten to less corrosive alkalis. The efficacy of this addition depends, in practice, on the conditions of aeration, for, in vigorous agitation, the sulphite may be unable to prevent access of oxygen to the metal. Alkaline detergents with a content of sodium sulphite are commercially available.

Although the addition of small amounts of oxidising agents can increase corrosion by alkalis very considerably, the addition of a sufficiency of such materials as permanganates, perborates or chromates can stop corrosion altogether. This has led to some confusion between the reported results of various experiments. Thus, while the accelerating effect of oxidising agents is stressed by some,[2] the addition of chromate[3] or perborate[4] is recommended by others. Clearly the use of oxidising agents to inhibit corrosion requires care and the quantity required must be ascertained for any application contemplated.

As for acid products, quiescent non-aerated alkaline materials can be packed in tin tubes or tin-plate containers. An additional measure of safety can be achieved by adding sodium sulphite to the material to absorb oxygen. Sometimes the alkalinity of a product can be kept below the threshold value for corrosion, e.g. milk of magnesia can have its pH adjusted by a citric acid addition, with some benefit in flavour.[5]

The main importance of the action of alkalis lies, however, in their use for cleaning, especially in the dairy industry. The precautions to prevent corrosion involve keeping aeration to a minimum, in which addition of sodium

sulphite can help, reducing the time of contact between solution and metal and thorough rinsing. A useful code of practice based on these principles is:

1. Clean as soon as possible after use, especially with milk products, in order to reduce the formation of strongly adherent deposits.
2. Use the mildest alkali consistent with the cleaning required.
3. Add sodium sulphite to the solution.
4. Minimize agitation of a type which drags in air.
5. Rinse thoroughly and quickly.
6. Avoid abrasives, which may remove tin mechanically.

Tin is anodic to steel in alkalis and if the two metals are in contact, the corrosion of the tin is likely to be accelerated. Since the steel cathode can evolve hydrogen, corrosion of the tin may be produced even in absence of oxygen.[13] It is therefore desirable that tin being cleaned in alkaline detergents should be kept out of contact with the steel container of the solution.

Chemical sterilisers such as hypochlorite or chloramine T. may corrode tin if used in high concentrations. At 100 p.p.m. of available chlorine, either of these compounds was found to be fairly safe, but at 200 p.p.m. was rather corrosive.[7] The addition of silicate to hypochlorite has been found advantageous.[8] If available chlorine concentrations cannot be kept under control, steam sterilisation is to be preferred for tinned equipment as it is not itself corrosive and leaves no residues.

Of basic materials other than compounds of the alkali metals, ammonia solutions have no action, but some amines have been reported to attack tin. Corrosion by fish packed in tinned containers has been stated to depend on the content of trimethylamine oxide,[6] although here the action may depend on the behaviour of the material as an oxidising agent, rather than as a base.[12]

REFERENCES

1. Kerr, R., J. Soc. Chem. Ind. (1935) **54**, 217.
2. Watts, O. P. and Whipple, N. D., Trans. Electrochem. Soc. (1917) **32**, 268.
3. Alder, U.S. Patent No. 1, 734, 706 (1929).
4. Little, L. L., Paper read before Am. Dairy Science Assoc. (1938.)
5. MacFarlan, R. L., J. App. Physics (1938) **9**, 576.
6. Jakobsen, F., Ronold, O. A. and Stokke, K., Tidenske Hermetikind. (1945) **31**, 47.
7. Haller, H. S., Grant, F. M. and Babcock, C. J., U.S. Dept. Ag. Tech. Bull. 736 (1941).
8. Botham, G. H. and Dummett, G. A., J. Dairy Res. (1949) **13**, 23.
9. Derge, G., Trans. Am. Inst. Min. Met. Eng. (1938) **128**, 391.
10. Derge, G. and Markus, H., Trans. Am. Inst. Min. Met. Eng. (1939), **133**, 294.
11. Ibid. (1941) **143**, 198.
12. Ronold, O. A. and Jakobsen, F., J. Soc. Chem. Ind. (1947) **66**, 160.
13. Britton, S. C., J. App. Chem. (1951) **1**, S132.

CORROSION BY NEAR-NEUTRAL AQUEOUS MEDIA

In neutral aqueous solutions, the oxide skin on tin usually prevents general corrosion, although the stifling of incipient corrosion at weak spots in the skin by precipitation of hydroxide may thicken it sufficiently to produce tarnish colours.

Distilled water is almost without detectable solvent action and block-tin pipes may safely be used in its preparation for purposes requiring a high-grade product. Some tarnishing occurs in hot distilled water by thickening of the oxide film, but this is not accompanied by loss of metal.

In solutions containing anions which form soluble tin salts, local break-down can occur with the production of small pits. This type of failure has become known as 'Black Spot' formation as the pits appear initially as black spots, usually surrounded by rings of tarnish colours. It may appear in some water supplies, in milk and in other products containing, by accident or design, salts such as chlorides, sulphates and nitrates. Chlorides appear to be most likely to stimulate the action. As corrosion proceeds a solid white product appears above the pits or streaming down from them. This consists principally of stannous oxide with about 20 per cent. of stannic oxide.[11]

Electrochemical measurements[1] have indicated the probable process of formation of the spots. Anodic attack of the metal, beginning at weak points in the oxide film, produces hydroxide and tends to heal the film. The anodic process, however, depletes the solution locally in OH ions and, if a spot is not healed in time, the solution may become, locally, sufficiently acid to permit the formation of a soluble anodic product. At such a spot, the film ceases to be in optical contact with the metal which is eaten away below it. The result is a spot reflecting no light and thus appearing black. In solutions containing anions forming insoluble tin salts, e.g. phosphate, borate and chromate, the anodic solution of the metal cannot occur and the spots are not formed.

Local corrosion has also been observed in solutions which deposit a scale on the metal and at points where the metal is in loose contact with another solid. Possible reasons are that the screening action of the touching solid produces differential aeration or that the protective skin on the metal becomes preferentially attached to the other surface. Tin, partly immersed in hot hard tap-water, was attacked locally at the water-line, where scale was deposited, but only a slight tarnish was produced in water otherwise similar but freed from scale-forming salts.[2] Nevertheless tin coatings on kettles and other vessels for hot water usually have a long life, the build-up of a firmly adherent scale over the whole immersed surface being probably in the long run protective.

Local corrosion, of the black spot type, although often removing a trifling weight of metal, can cause deep penetration, sufficient to make a gap in a tin coating or even to perforate a collapsible tin tube. Fortunately, the action reaches a destructive stage infrequently, even when chlorides are present, possible reasons being the presence of other salts tending to heal defects in

the oxide film and that many surfaces may have only easily reparable defects in their film.

It is clearly desirable that the tin surface shall be as free as possible from scratches and other defects, especially any produced immediately before contact with a possibly corroding material. Sometimes, particularly for packs in tin tubes, freedom from contamination by injurious salts, such as chlorides, may be sought in order to avoid any risk of local corrosion. When this is not possible, a slight elevation of the pH or the addition of sodium phosphate may be useful. A further preventative measure, found successful in the dairy industry, and applicable to tinned vessels in other uses[11] is to immerse in the liquid contained in the vessel a zinc or aluminium surface in electrical contact with the tinned surface. The tin, acting as cathode to the second metal, is protected, but the other metal is corroded and will of course contribute some contamination to the contents of the vessel. Conversely, some instances of corrosion of tin coatings have been attributed to their contact with a metal cathodic to them, e.g. nickel-plated immersion-heater sheaths in tinned kettles and tin tubes in bare copper tanks. It is a wise precaution to have all surfaces tinned, except when an anodic metal is deliberately used to protect tin.

Sea-water produces a slow corrosion which gradually spreads over the whole surface, the spread being possibly assisted by scale deposition. Tin bars, exposed for four years to sea-water with total immersion for 93 per cent. of the time, lost weight equivalent to an average penetration of 0·00003 in. per year for 99·2 per cent. tin and 0·00009 in. per year for 99·75 per cent. tin.[3]

The effect of a great variety of near-neutral aqueous materials on tin or on heavy tin coatings is in accord with the outlines of behaviour just given, i.e. it is normally extremely slight, but occasionally, in unfavourable circumstances, local corrosion may be produced. The presence of sulphur compounds may cause staining, an effect of which is discussed in a later section (p. 27). Special mention may be made of some materials which have special requirements or which do not obviously fall into the category of neutral solutions.

It is undesirable that drugs should be contaminated by metal or otherwise have their character changed by their containers. Solutions of many drugs were found to contain no dissolved or suspended tin salts after contact with tin for ten hours at 95° C.[5] The materials examined included hydrochlorides of morphine, atropine and cocaine, strychnine nitrate, novocain, and mixtures of caffeine with sodium benzoate and with sodium salicylate. The long-period storage of morphine sulphate solution in tin tubes was found to produce a haziness resulting from slight corrosion of the metal, and, although the drug seemed unaffected, the use of alternative salts of morphine was explored as a means of avoiding any doubt.[7] Acetate, citrate and lactate and tartrate were all less liable than sulphate to produce the haze and tartrate was without effect after long storage.

Photographic developing solutions are also stringent in their requirements and unfortunately, if they pass over tin, they may pick up sufficient metal

to cause fogging, a tendency increased if the tin is in contact with a more noble metal.[4]

Formaldehyde solutions used extensively in the plastics industry are required to have low contents of heavy metals. Traces of formic acid tend to make them corrosive to many metals, but tin is unaffected by them, and well-tinned copper is considered suitable for vessels and pipes used in their manufacture.[9]

The maintenance of clarity and colour in wine was found to be adversely affected by contamination with tin.[10] As little as 3 mg. per litre caused some discoloration in red wines and turbidity in white wines, and tin had not a resistance to corrosion adequate to ensure that this limit was not exceeded.

The strong hydrogen peroxide solutions used in rocket propellants must not corrode the metals with which they come into contact and must not have their stability affected by them. Tin was one of the metals found satisfactory.[8]

Tin was affected less than other metals when kept for 36 weeks at various humidities at room temperature in contact with various leathers, tanned with either organic or inorganic materials.[6]

The effects of sulphur-containing compounds and of dairy products are dealt with separately.

REFERENCES

1. Hoar, T. P.. Trans. Faraday Soc. (1937) **33**, 1152.
2. Hoar, T. P., J. Inst. Met. (1934) **55**, 135.
3. Friend, J. N., J. Inst. Met. (1928) **39**, 111.
4. Crabtree, J. I., Hartt, H. A. and Mathews, G. E., Ind. Eng. Chem. (1924) **16**, 13.
5. Jermstad, A. and Gaule, A., Schweitz. Apoth. Ztg. (1919) **57**, 89.
6. Innes, R. F., J. Internat. Soc. Leather Trades Chem. (1935) **19**, 5.
7. Christiansen, W. G. and Jurist, A. E., J. Am. Pharm. Assoc. (1943) **32**, 209.
8. Bellinger, F., Friedman, H. B., Bauer, W. H., Eastes, J. W. and Bull, W. C., Ind. Eng. Chem. (1946) **38**, 310.
9. Homer, H. W., J. Soc. Chem. Ind. (1941) **60**, 215.
10. Searle, H. E., La Que, F. L. and Dohrow, R. H., Ind. Eng. Chem. (1934) **26**, 617.
11. Brennert, S., Black Spots on Tin and Tinned Ware, Tin Res. Inst. Pub. D.2 (1935).

ADDITIONAL BIBLIOGRAPHY

Corrosion products of ancient tin specimens after prolonged interment or immersion:

Bannister, C. O., J. Inst. Met. (1936) **35**, 71.

Smythe, J. A., J. Inst. Met. (1940) **66**, 355.

CORROSION BY MILK PRODUCTS

Since there is little effect of milk products and tin on one another, tin-coated equipment is used very extensively in the dairy for transport, processing and storage. Further reference will be made to the behaviour of imperfect coatings in Part III, but much of the equipment used is heavily coated with tin and the performance of tin itself in contact with products handled is more important in practice.

Some results of tests of tin, partly immersed in quiescent milk, presented in Table VII, show that even sour milk has only a slow effect on the metal at ordinary temperatures.[2]

Such small quantities of tin as find their way into the milk are without effect—unlike some other metals, notably copper, which, by catalysing oxidising actions, produce an oily taint.

TABLE VII

CORROSION OF TIN, PARTLY IMMERSED IN QUIESCENT MILK

Product	*Temperature* °F.	*Duration of Test*	*Weight loss as mg. per sq. dm. per day*
Fresh milk ..	70	5 days	1·5
	145	5 hours	6·7
Sour milk ..	98	5 days	2·4
	70	2 days	1·1
Fresh cream ..	70	5 days	0·2
	145	5 hours	11
Sour cream ..	70	5 days	0·6
	145	5 hours	6·7
Sour neutralised cream ..	145	5 hours	11

Sometimes, local action by milk products is observed, black spots being produced as described for neutral aqueous solutions (p. 23). It occurs only occasionally, tending to happen quickly or not at all. No doubt the initial condition of the surface determines this very largely and the presence of scratches or other surface imperfections in a new coating will be favourable to the start of the action. A means of prevention for dairy plant is to give cathodic protection by introducing a zinc or aluminium surface, bonded to the tinned surface.[1] (p. 23).

The largest source of loss of tin in the dairy industry is probably cleaning. Mention has already been made of means of reducing loss in washing with alkaline detergents (p.21), of the possible use of weak organic acids as less corrosive cleaning agents (p. 19) and of the need for caution in using strongly acid cleaners (p. 16). To these recommendations may also be added the desirability of avoiding the use of harsh abrasives, which may remove appreciable amounts of tin, a relatively soft metal, and may also leave scratches that provide possible sources of local corrosion.

Tin foil provides a very good wrapping material for processed cheese. For this purpose it is well suited by its good tarnish resistance on both faces and also because it clings to the cheese very much better than does its competitor in this field, aluminium, and thus achieves a good seal. Uncoated tin-foil may sometimes be discoloured. Investigation[3] has shown that the emulsifying agent used in preparing the cheese may influence this, phosphates being specially liable to promote tarnishing, especially if the acidity of the product is less than shown by a pH value of less than 5·8. A thin transparent lacquer may be applied to the cheese side of the foil. This prevents discoloration without affecting the cling of the foil to cheese.

Discoloration of the tin coating in cans of cream has been shown[4] to result from the breakdown of proteins during processing to give active sulphur compounds. Measures recommended to avoid this were the avoidance of the use of abnormal milks, the reduction of heat treatment time to the least necessary for sterilisation, and the use of a minimum quantity of stabiliser. For the stabiliser, sodium bicarbonate was found to be preferable to sodium phosphate or sodium citrate.

REFERENCES

1. Brennert, S., Black Spots on Tin and Tinned Ware, Tin Res. Inst. Pub. D2 (1935).
2. Hunziker, O. F., Cordes, W. A. and Nissen, B. H., J. Dairy Sci., (1929) **12**, 140.
3. Templeton, H. L. and Sommer H. H., J. Dairy Sci. (1937) **20**, 231.
4. Jackson, J., Howatt, G. R. and Hoar, T. P., J. Dairy Res. (1936) **7**, 284; (1937) **8**, 324.

CORROSION BY SULPHUR COMPOUNDS IN AQUEOUS SOLUTION

Sulphur itself has no action on tin at ordinary temperatures, but the two elements react vigorously if heated together. Many sulphur compounds will, however, in neutral or feebly acidic aqueous solution, produce surface stains of sulphide, although the loss of metal is trifling. This is not confined to products

containing sulphur as sulphide, for other sulphur compounds become reduced at the metal surface. Dilute sulphurous acid will, for instance, produce tarnish colours and sometimes may give black deposits of sulphide. This may happen with products containing sulphur dioxide added as preservative.

Many food products, e.g. meats, soups and some vegetables, containing organic sulphur, also produce stains of sulphides of tin.[1] The action is usually only sufficient to produce thin films showing interference tints. The film remains on the metal, but even the discoloration may be objectionable on a container for foodstuff. It can be overcome by the application of lacquers, sometimes pigmented with sulphur-absorbent material and, better, by a simple chemical treatment of the tin. This, the 'Protecta-Tin' process,[2] requires brief immersion of the tin or tinned surface in a hot alkaline chromate solution. The process also confers some rust resistance on discontinuities in tin-coatings on steel, an aspect which will be referred to in Part III (pp. 48 and 53).

Thin films produced by sulphur compounds have been held by some to be protective.[4] Certainly they do not thicken rapidly and sheets of tin are used to separate sheets of ebonite during the curing process. The sheets may be used many times since the tarnishing has little effect on the good surface finish required to confer its likeness on the product.

The effect of sulphur compounds on the corrosion of tin-coated steel in acid media can be more serious; this matter is dealt with in Part III (p. 51).

REFERENCES

1. Mantell, S. E. and Lincoln, E. S., Canadian Chem. Met. (1927) **11**, 29.
2. Anti-rust and Anti-stain Treatment of Tinplate (the 'Protecta-Tin' process). Tin Res. Inst. Pub. TCN. 1950.
3. Dickinson, D., Food (1948) **17**, 20.

CORROSION BY NON-AQUEOUS MEDIA

In general, water-free materials, excepting the halogens, have little effect on tin at ordinary temperatures. Lubricating oils, drying oils, organic solutions and refrigerants can usually be handled in tin-coated metal. The presence of water, especially if accompanied by acidic decomposition products of materials such as chlorinated solvents, can lead to corrosion, the extent depending on the degree of contamination. In pure carbon tetrachloride, the average rate of corrosion during a six months' test was 0·7 mg./sq. dm./day at room temperature; in a mixture with water at the boiling point corrosion was at the rate of 5·6 mg./sq. dm./day.[7]

Common petroleum products have a very slight action on tin and the metal does not promote deposition of gummy products as do some other metals,

notably copper. Tin coated steel was found to be unattacked by a variety of fuels, such as petrol, alcohol and benzine,[2] or alcohol/petrol mixtures.[3 4] As with solvents, it is possible for contaminants to induce corrosion,[5] sulphur compounds present together with water being a possible source of trouble.

The inclusion of water in mineral oil can produce some corrosion,[6] although the water-free oils soon produce a protective film on the metal.[7] Olive oil and peanut oil also were found to have a slight initial action which soon ceased.[6] No reaction between tin and alcoholic solutions of essential oils was found during prolonged storage.[8 9]

Solutions of acetic, propionic, butyric, lauric, palmitic and stearic acids in benzene were found to have no action on tin, with the exception of a very slight effect by acetic acid.[12]

Tin was found to be unaffected by methanol even when 20 per cent. water was added with and without additions of 2 per cent. formaldehyde or 1 per cent. formic acid.[11]

Carbon disulphide has no action other than the production of a tarnish film.

An instance of corrosion of tin pipes by liquid and gaseous sulphur dioxide has been reported.[10] A crystalline solid was found having the composition SnS_2O_4 (stannous hyposulphite) and giving the reactions expected of such a compound. This action is surprising for anhydrous sulphur dioxide appeared to have no action in tests and the presence of moisture in the corroded installation could not be substantiated. In view of the low temperature involved, a preliminary allotropic change in the tin is a possibility, although practical examples of this change are very rare.

REFERENCES

1. Rhodes, F. H. and McCarty, J. T., Ind. Eng. Chem. (1925) **17**, 909.
2. Dietrich, K. R., Korr und Met. (1929) **5**, 110.
3. Fritzweiler, Auto-Technik (1925) **14**, 13.
4. Graempe, M., Oel u. Kohle (1935) **11**, 118.
5. Wood, A. D., Sheely, C. and Trusty, A. W., Ind. Eng. Chem. (1925) **17**, 798.
6. Haringhuizen, P.S. and Was, D. A., Proc, K. Akad. V. Wetenschappen, Amsterdam (1938) **41**, 62.
7. Haringhuizen, P.S. and Was, D. A., Proc. Akad. Sci. Amsterdam (1936) **39**, 201.
8. Rosenberger, G. A., Seifensieder Ztg. (1937) **64**, 967.
9. Devey, J. D., Soap, Perfumery and Cosmetics (1942) **15**, 329.
10. Cooke, W. T., Austral. Chem. Inst. J. and Proc. (1939) **6**, 58.
11. Guillemin, A., Ann. Chim. (1944) **19**, 145.
12. Dubrisay, R., Chim. Ind. (1940) **44**, 277.

EFFECT OF IMPURITIES IN TIN

In the preceding sections, the results quoted have usually referred to metal without deliberate alloying additions, but possibly containing small amounts of impurities. Adventitious impurities, the commonest being antimony, although not affecting the general trend of behaviour, sometimes have a perceptible effect on the speed of corrosion.

Reference has been made (p.24) to long term tests in sea-water in which 99·75 per cent. tin suffered a weight loss of, at one situation, about thrice and, at another, about twice that suffered by a less pure tin containing 0·3 per cent. of antimony and 0·4 per cent. of lead[1]. The purer metal appeared to be more prone to pitting. When samples of the same metals were exposed to an industrial atmosphere for seven years, the more pure metal lost less weight than the other[16].

In citric acid solutions (0·5 and 1 per cent.) in presence of air, an impure tin containing: copper, 0·41 per cent.; antimony, 0·25 per cent.; lead, 0·13 per cent., and iron, 0·035 per cent., was corroded up to 15 per cent. more slowly than samples containing 99·95 per cent. and 99. 88 per cent. of tin, an effect attributed to the presence of antimony.[2] Pure (99·99 per cent.) tin was corroded rather faster by 0·1 M. solution of hydrochloric or citric acid than a commercial grade having as its main impurities 0·225 per cent. of antimony, 0·039 per cent. of lead and 0·021 per cent. of bismuth.[14] The two materials behaved similarly when immersed in various domestic supply waters. Antimony present in amounts as small as 0·01 per cent. was found to increase the rate of solution of tin in concentrated hydrochloric acid and in 10 per cent. ferric chloride solution, but bismuth reduced it.[4] The results just quoted and others cited below indicate however that, in corroding media of greater practical importance, the presence of either of these elements in tin is usually beneficial.

Deliberate small alloying additions, especially of copper or antimony, are made in order to produce greater hardness of tin foil. Other additions have been made experimentally in attempts to improve corrosion resistance or mechanical properties.

In dealing with atmospheric corrosion (p. 14), results in Table I, for alloys with small contents of copper and antimony, show that 2·2 per cent. of antimony had no appreciable effect and 0·2 per cent. of copper had a slight adverse effect over a long period of exposure.[3]

Corrosion by 0·5 per cent. citric acid, in presence of air, was reduced by addition of either antimony[5] or bismuth[2]. While 0·25 per cent. and 0·5 per cent. of antimony reduced corrosion by 8 per cent. and 11 per cent. respectively, increased additions produced no further effect. Bismuth additions reduced corrosion slightly more. (See also p.33 for the effect of larger additions of antimony). Antimony or copper additions slightly increased corrosion in sodium carbonate solution, copper producing a rather larger effect.[15]

Aluminium, magnesium and zinc have been reported as harmful impurities in some environments, although only aluminium has an effect of known practical importance.

The presence of small amounts of aluminium in tin is certainly extremely deleterious for exposure to moist conditions. A micro-constituent containing aluminium is selectively and rapidly corroded, leading to inter-crystalline embrittlement.[6] Aluminium-tin alloys were found to suffer surface embrittlement on standing in air and alloys with up to 50 per cent. of aluminium decomposed water, with evolution of hydrogen.[13] The exclusion of aluminium from tin used to produce foil is therefore of great importance. Aluminium-tin bearing metals have, however, been used successfully in internal combustion engines.

Alloys of tin with up to 5 per cent. of magnesium were rapidly corroded in water, [8 15] and were considered to be unsuitable for any moist environment. The presence of 0·1 per cent. of magnesium appeared to be tolerable.[15]

The presence of zinc in fusible tin safety plugs for steam boilers was condemned as leading to the formation of a network of corrosion product that could obstruct the functioning of the plugs.[7] Additions of zinc, of up to 15 per cent., were said to cause intercrystalline corrosion in the atmosphere,[15] but other work casts some doubt on this. It is certain that zinc is not a harmful addition to tin in all amounts in many environments. Alloys of tin with 8–20 per cent. zinc were found to be quite suitable as capping foils for milk-bottles[9] and the good corrosion resistance of electro-deposited tin-zinc alloy is used to provide protective coatings (p. 71).

It has been found recently that additions of as little as 0·1 per cent. of indium, zinc or phosphorus to tin exercise a remarkable restraint on the thickening of the oxide film when the metal is heated in air. These indium and zinc additions also prevented tarnishing in hot water, but did not prevent 'black spot' formation in chloride solutions and did not increase resistance to dulling in condensed moisture. It has been reported that larger additions of indium, a 'few per cent.', prevent local corrosion in sodium chloride solution[10] and that additions of 0·5–3 per cent. improved resistance to sodium carbonate solution [11 15]. Zinc additions of 0·1 per cent. upwards also were beneficial in alkaline solutions, being notably effective in raising the minimum pH value for corrosion to begin in sodium carbonate solution.[15] This last-mentioned effect seemed to be associated with the production of a carbonate film and, in caustic soda solution, it was not observed.

Studies of the effect of grain-size of tin on corrosion by sodium carbonate solution showed the weight-loss was less for finer grained material, grain boundaries being less attacked than the grains.[12] This was true of 99·99 per cent. tin as well as for tin containing 1 per cent. copper, but the grain refinement brought about by some alloying elements was considered to contribute to their effect on corrosion.[15]

REFERENCES

1. Friend, J. N., J. Inst. Metals (1928) **39**, 111; (1932) **48**, 109.
2. Morris, T. N. and Bryan, J. M., Food Inv. Board, D.S.I.R., Spec. Rep. No. 44, 1936, p. 13.

3. Kenworthy, L., Trans. Faraday Soc. (1935) **31**, 1331.
4. Kutzelnigg, A., Z. Elektrochem. (1935) **41**, 450.
5. Bryan, J. M., Ann. Rep. Food Inv. Board, D.S.I.R., 1934, p 179.
6. Heyn, E. and Wetzel, E., Mitt. Kaiser-Welhelm Inst. Metallforsch. (1922) **1**, 19.
7. Burgess, C. and Merica, P.D., Bur. Standards Tech. Paper 53, 1915.
8. Tin and Its Uses (1940) No. 4, p. 8.
9. Kerr, R., J. Soc. Chem. Ind. (1942) **61**, 128.
10. Fink, C. G., Jette, E. R. Katz, S. and Schnettler, F. J., Trans. Electrochem. Soc. (1939) **75**, 463.
11. Derge, G., Trans. Electrochem. Soc. (1939) **75**, 469.
12. Ibid. p. 449.
13. Hanson, D. and Sandford, D. J., J. Inst. Met. (1935) **56**, 196.
14. Hoar, T. P., J. Inst. Met. (1934) **55**, 135.
15. Derge, G. and Markus H., Trans. Am. Inst. Min. Met. Eng. (1941) **143**, 198.
16. Friend, J. N., J. Inst. Met. (1929) **42**, 149.

Part II
ALLOYS OF TIN

PEWTER AND BRITANNIA METAL

Pewter alloys have a long history, in the course of which the compositions used have varied somewhat. Old pewters contained often a substantial proportion of lead. Their behaviour depended on composition, although all had good resistance to serious corrosion. The lead-containing alloys could, however, contribute undesirable amounts of that metal to beverages contained in them and modern alloys are lead-free.

The alloys now produced contain antimony and/or copper, with a total of alloying elements up to 10 per cent. Some authorities term them 'Britannia metal', reserving the word 'Pewter' for the old lead-containing alloys. Britannia metal is however also used as a name for ware produced from the alloys and silver-plated. The intention here is to deal with the unplated alloys. These are used extensively in the production of decorative ware for domestic use. In this service, the retention of a bright appearance is prized rather more than the development of the dull metallic lustre which makes old pewter attractive.

The alloys in general behave very much like tin, but their resistance to dulling in the atmosphere is slightly less. In the reflectivity measurements referred to in discussing tin[1] (p. 13), Britannia metal showed a slightly greater decline in brightness than did tin when subjected to periodic washing, but lost brightness similarly when not cleaned.

The action of near neutral solutions resembles that on tin,[2] black spot formation and local corrosion under scale deposits being possible. Tin, with 5 per cent. antimony only, was found less liable than unalloyed tin to attack under scale deposits, but the extra addition of 1 or 3 per cent. of copper cancelled this benefit. The addition of 5 per cent. antimony to tin, with or without 1 or 3 per cent. copper, reduced corrosion in 0·1 M. hydrochloric acid, but was without effect in 0·1 M. citric acid. (cf. p.30) Resistance to atmospheric corrosion and to water supplies is the primary requirement of these alloys in their usual applications, although the action of acids is of interest for the tin-antimony alloys whose use as solders may bring them into contact with more severe conditions.

REFERENCES

1. Kenworthy, L. and Waldram, J. H., J. Inst. Met. (1934) 55, 247.
2. Hoar, T. P., J. Inst. Met. (1934) 55, 135.

SOLDERS AND FUSIBLE ALLOYS

Alloys of tin, usually with lead but also with silver and antimony, are used extensively as solders to make joints in other metals. The compositions of the alloys used and the processes employed in their use have been fully described in another publication.[1] Some reference must however be made here to the soldering process since an important source of corrosion trouble associated with soldered joints may be developed by it.

Corrosion by soldering fluxes

In making a soldered joint, a flux is used to clean and to keep free of oxide the surfaces being joined. Fluxes, being by nature oxide removers, are frequently somewhat corrosive and, if residues of them are not removed when the work is completed, damage to the metal may follow. This may not be confined to the joint for, during soldering, metal well away from the joint may be spattered. The action of flux residues is probably the largest source of corrosion troubles associated with soldered joints. Desirable precautions against it are to wash away flux residues when possible and, especially if washing is not possible, to choose a flux which, although adequate for the work, is least likely to leave a corrosive residue.

The commonly used spirits of salt (hydrochloric acid) and killed spirits (zinc chloride) are very likely to leave hygroscopic and corrosive residues which should be completely washed away. The whole article should be rinsed, especially when spirits of salt has been used, to remove effects of spray and fume. In rinsing after the use of a zinc chloride flux, it is advisable to rinse first in hot water acidified with a little hydrochloric acid, in order to avoid the formation of insoluble basic zinc salts which may happen with the untreated water supply. This acid rinse is followed by a thorough rinse in water to which a little soda may be added.

Resin is safe, being active at soldering temperature but inert at normal temperatures, but it is in general not sufficiently vigorous and is usually activated by additions of acidic compounds. The addition of weak acids, such as oleic or lactic acids, has been employed, but cannot be considered free from risk of causing corrosion. Salts of organic bases are better, since they decompose when heated and should leave a harmless residue. Examples are the hydrochlorides of aniline, naphthylamine and hydroxylamine, and naphthalene tetrachloride.

Phosphoric acid is a useful flux on steel, copper and brass. It leaves a glassy residue, which, though usually protective, cannot be always relied on. Aniline phosphate has been found safer and a mixture of aniline, 51 ml; phosphoric acid, 34 ml; ethylene glycol, 40 ml was found to be an effective flux, even on metals difficult to solder with zinc chloride, without leaving corrosive residues.[2]

Solution containing urea and glutamic acid hydrochloride has been found to be a very effective flux, which, although slightly corrosive in its raw state, leaves non-corrosive residues.[3] The solution is saturated with the acid and contains sufficient urea to neutralise it. The neutralisation is not, however,

complete until the flux is heated as it is in the soldering process, so that to be sure of freedom from corrosion, the flux should not be allowed to wet areas outside the heated zone.

The choice of a flux has, in practice, to be determined by the nature of the metals to be joined, the possibility of removing flux residues, the importance attached to possible corrosion and the need for rapid output. In making a decision it should be remembered that the use of less active fluxes can often be made possible by 'tinning' beforehand the parts to be joined with tin or tin-lead, using electrodeposition or hot-dipping.

The requirements for security from corrosive residues are indicated by the provisions of Ministry of Supply Specification D.T.D. 599 for non-corrosive flux. These call for a flux consisting of a high grade resin and a small constant proportion of an agent to facilitate soldering. It must not contain more than 0·5 per cent. (or 0·7 per cent. for cored solder wire) of halide in the non-volatile matter and must contain no other residue which would render flux, flux residues or volatile matter corrosive, hygroscopic or otherwise unsuitable. A test of exposure of soldered copper in a humidity chamber for 24 hours is prescribed to reveal any deficiency.

Corrosion of soldered joints

In service, the soldered joint usually presents to corrosive environments a comparatively small area of solder within a larger area of another metal. The behaviour of solders when exposed in contact with another metal is therefore the most important aspect of their corrosion resistance, although coatings of tin-lead alloy have important applications (p. 68).

Solders are anodic to copper, but a wide experience shows that this is only a source of trouble in conditions which give high conductivity of the solution in contact with the joint, and no opportunity for the formation of beneficial obstructive layers on the metal surfaces. Thus, joints made with 50/50 lead-tin solder in copper pipes are widely used without complaint in a variety of domestic water supplies, but in sea-water and some chemical solutions, including photographic solutions, some destructive action is likely.

One occasional casualty in domestic water supplies is the copper ball of cistern valves. Solder in the seam of the ball or the junction between ball and arm may be corroded. The conditions here are rather special, the joint being continuously wet and well aerated. The trouble is said to be particularly likely in waters high in chloride which may also affect the seams of copper hot-water storage cylinders.[4] The risk can be reduced by employing solders of high tin content, a solder with 85 per cent. tin being found in laboratory tests to be resistant.[5]

The formation of a streak of copper/tin compound with high nobility has been reported to produce local corrosion in soldered copper roof, but this appears to be an unusual occurrence, due to overheating in making the joint.[6]

Soldered brass seldom gives trouble; it is extensively used in domestic water supplies and in the radiators of automobiles. In radiators, anti-freeze solutions have been alleged to cause corrosion, possibly because such materials

as glycol and glycerine sometimes detach deposits from the metal, although the addition of inorganic salts as impurities may contribute. The addition of sodium nitrite, valuable as a corrosion restrainer for other metals, increases corrosion of soldered joints, but sodium benzoate is safe and can protect against the action of nitrites.[7] Satisfactory protection of cooling systems with cast iron cylinder blocks and soldered copper or brass radiators against the action of 20 per cent. glycol solutions has been obtained by the combined addition of 1·5 per cent. sodium benzoate and 0·1 per cent. sodium nitrite.

Solder has a slight and variable electrode potential difference from tin itself and soldered joints in tinned ware are seldom subject to special corrosion. This is of great practical importance in view of the wide use of tinned surfaces for handling foodstuffs, which, although they can safely hold tin, must not absorb lead. (The permissible U.K. limits are 286 p.p.m. for tin and 1·4 p.p.m. for lead). Safeguards are to minimise the area of solder exposed to foodstuffs and, when the area is inevitably large, as in rounding out corners and crevices of large vessels, to use high tin (preferably at least 60 per cent.) solders.

The restriction of the exposed area of solder is practised to a high degree in the manufacture of the cans used for foodstuffs. About 80 per cent. of these are an 'open top' type for which solder is only applied outside a double folded seam. For milk, a 'slip-ended' can may be used with both ends soldered and with a final seal by a single spot of solder. In American tests,[8] the pick-up of lead by evaporated milk was found to be negligible, even when solder pellets were deliberately introduced inside the cans. Sardines were found to pick up negligible amounts of lead from the soldered joints of cans, even when these were not well made, and instances of lead being found in them were traced to the improper substitution of tin-lead for pure tin coatings on grills used to cook the fish before canning.[16]

Soldered joints in iron or lead are usually cathodic to the metal. For lead, the effect appears to have no practical significance and ferrous products are normally protected in any case for exposure to corrosive environments.

Tin-lead solders are cathodic to zinc and in a moist environment a zinc coating in steel may be corroded at an increased rate near soldered joints with rusting of the steel following in due course. The action may be accelerated by local destruction of the coating by flux during the soldering operation. The use of solder in making joints in galvanised sheet for ducts of air-conditioning plant was found to be inadvisable.[15] Apparently the source of trouble was the injury to the coating for the method found satisfactory was carbon arc welding using tin-coated Everdur filler rods, which left a tin coating on the joint zone and thus did not avoid a cathodic joint.

Solder was found to be anodic to Monel metal in water at 200° F. and the corrosion of joints was accelerated, but at 150° F., no special corrosion was observed.[9] Soft soldered joints are not generally considered satisfactory for use with this alloy in corrosive environments.

The difficulties of soldering aluminium are well known and soft soldered

joints in this metal are usually avoided. When they have to be made, corrosion of the metal around the joint is always likely. Possibly tin-zinc solders may be less likely to produce an injurious combination than others, but it is a wise precaution to apply a protective covering to any soldered aluminium that may be exposed to moist conditions.

Fusible alloys

Solders are only one group of the fusible tin alloys. There is also a large range of alloys whose uses primarily depend on their relatively low melting-points. The compositions, properties and uses of this group have been described in another publication.[10] For many alloys within it, corrosion resistance, other than that they shall not oxidise unduly on melting, is not of prime importance. For those used in safety devices stability of form is however usually essential.

Little comparative information on oxidation rates of the molten alloys is available, but attention has been drawn to the beneficial effects of indium additions.[11] These markedly reduce the oxidation of the lead-tin-cadmium-bismuth alloys.

The fusible alloy cores of safety plugs fitted to steam-boilers are not usually corroded on the water-side, but deposits of ash or of salts from water that has leaked to the fire-side may react with the alloy to produce hard layers of high melting-point capable of obstructing the proper functioning of the plug.[12] A remedial measure is to ensure good bonding of core to plug, thus avoiding a possible source of water leaks, but frequent inspection is a very desirable safeguard. When waters corrosive to the plug-filling are encountered, copper-plating of the water-end has been found useful.[13]

When strips of fusible alloy are used in fire-alarm systems, the difficulty mentioned in connection with fuse wires (p. 6) of an oxide layer holding the molten alloy together may arise. The alloys are usually not as resistant as tin to oxidation on heating and a suitable tension device to ensure their rupture on melting may be necessary.

The tin-containing amalgams used as dental fillings may appropriately be mentioned in this section. Little is known about the effects of their composition on resistance to discoloration in service, but these appear to be insufficiently large to cause interference with a choice of material based on the other properties required. The polishing of the filling is considered to be a desirable safeguard against discoloration, but the retention of a clean metallic surface by these materials is a matter of common experience. Contact of amalgam filling with a more noble metal, e.g. with gold wire or with gold restorations of opposing or adjacent teeth, has been considered to cause discoloration.[14]

An interesting corrosion trouble has been observed in amalgams containing more than about 0·5 per cent. zinc. If, during preparation, these amalgams come into contact with moisture, even the perspiration of a hand, some hydrogen is liberated and has the effect of causing the restoration to expand.[14] The 'mulling' of the amalgam in the bare hand is therefore inadvisable. Once the amalgam has hardened it is resistant to corrosion.

REFERENCES

1. Lewis, W. R., Notes on Soldering, Tin Res. Inst. Pub. HN. (1948).
2. Willstropp, J. W., Sidery, A. J. and Sutton, H., J. Inst. Met. (1936) **59**, 53.
3. Strader, J. E., U.S. Pat. 2,470,957, 24/5/49.
4. Kenworthy, L., J. Inst. Heat and Vent. Eng. (1940) **8**, 2.
5. Homer, C. E., Tin and Its Uses, No. 12 (1942) 1.
6. Merica, P. D., Chem. Met. Eng. (1917) **16**, 657.
7. Vernon, W. H. J., Wormwell, F., Ison, H. C. K. and Mercer, A. D., Motor Ind. Res. Assoc. Bull., Fourth Quarter (1949) **19**.
8. J. Ind. Hygiene and Toxicology (1937) **19**, 491.
9. MacKay, R. S. and Worthington, R., Corrosion Resistance of Metals and Alloys (1936) Reinhold Pub. Corp., New York, p. 206.
10. Fusible Alloys Containing Tin, Tin Res. Inst. Pub. No. TRE (1949).
11. French, S. J., Ind. Eng. Chem. (1935) **27**, 1464.
12. Freeman, J. R. Scherrer, J. A. and Rosenberg, S. J., Bur. of Standards J. Res. (1930) **4**, 1.
13. Turner, T. H., J. Inst. Loco. Eng. (1945) 154.
14. Worner, H. K., Austral. J. of Dentistry (1943) 157.
15. Eckberg, A. R., Met. Progress (1939) **36**, 633.
16. Lampitt, L. H. and Rooke, H. S., Analyst (1933) **58**, 733.

BEARING METALS

Alloys of tin with lead, copper and antimony, the so-called Babbitt alloys, are extensively used in lubricated bearings. Their composition, mechanical properties and applications have been considered in another publication.[1]

So long as these alloys were almost the only ones used to line bearings, little was heard of corrosion in those bearings to which water had no access. Since, for mechanical reasons, other alloys have been introduced, bearing corrosion has needed investigation, and sometimes the Babbitt alloys have been compared with the newer materials. For example, tests[2] using the Underwood apparatus,[3] in which hot lubricating oil is sprayed on to bearing shells, included Babbitt alloys (both high tin and high lead) with copper/lead and cadmium base alloys. Corrosion, measured both by loss of weight of the bearing and by changes in properties of the oil, was negligible with the high tin alloys at temperatures of 325, 350 and 375° F. and only moderate with the lead Babbitts, but was severe with the other alloys. Again, tests in neutral minerals oils at 80° C. showed that tin-rich and lead-rich Babbitts were not affected, but attempts to substitute other metals for tin in the lead-rich alloys resulted in corrosion.[4]

An important point also is that tin and lead act as anti-oxidants in the oil and any slight corrosion reduces sludge formation, in contradistinction to the action of copper.[5]

Aluminium/tin bearing alloys have useful properties for service in internal combustion engines.[6] No publication of any corrosion trouble with these alloys is known to the author and it is presumed that, when lubricated, they lose the reactivity with moisture which characterises aluminium-tin alloys in general (p. 31).

When water can gain access to any bearing, some corrosion may occur. It may affect the bearing metal itself, the shell or the journal or all three, depending on their electrochemical relationship. The severity of the action depends on what the water carries in solution and on what it can extract from the lubricant.

In some marine bearings, salt water may be damaging. Dosage of the incoming water with sodium nitrite has been found in such situations to restrain corrosion of bearing metal and journal.[7]

Special bearing alloys may be necessary for situations with free access of salt water and promising results have been reported for an alloy suited to tail-shaft bearings.[8] This, a tin-antimony-cadmium alloy, was shown in laboratory tests to have high intrinsic resistance to corrosion by sea-water, to be almost equipotential with steel in sea-water and to have satisfactory bearing properties, including a high resistance to seizure when tested in absence of lubricant. Trials in sea-going ships have confirmed the good corrosion resistance.

REFERENCES

1. Forrester, P. G., Babbitt Alloys for Plain Bearings, Tin Res. Inst. Pub. TSH, 1947.
2. Tichvinsky, L. M., S.A.E. Journal (1943) **51**, 69.
3. Underwood, A. F., A.S.T.M. Symposium on Lubricants (1937), 29.
4. Korr. u. Met. (1936) **12**, 50. Communication from the Deutsche Arbeitanschuss Nichteisenmetalle.
5. Haringhuizen, P. S. and Was, D. A., Proc. K. Akad. Wet. Amsterdam (1937) **40**, 39.
6. Hives, E. W. and Smith, F. H., S.A.E. Journal (1940) **44**, 106.
7. Hoar, T. P., J. Soc. Chem. Ind. (1950) **69**, 356.
8. Hedges, E. S., Tin and its Uses (1941) No. 10, 5.

COPPER-TIN ALLOYS

An alloy of copper with about 32 per cent. of tin was found in ancient times to provide a material, which although somewhat brittle, could take a high polish giving reflecting qualities nearly equal to those of polished silver and more

durable. Such alloys were used in the production of mirrors—the 'speculum' of the Romans—and have become known as speculum metal. Although replaced by metal-backed glass for mirrors in domestic use, they are still used in optical instruments.

Speculum alloys can be easily electrodeposited and, in recent times, it is as a coating that they have been most widely used. They will therefore be dealt with more fully in Part III (p. 74).

Although bronzes are generally regarded as copper alloys, it may not be out of place to point out some of the benefits of alloying copper with tin. The effect of the tin addition is to produce a metal of much better mechanical properties, easy to cast and work, never more than slightly impairing and sometimes improving the corrosion resistance. The usefulness of bronzes in offering a high strength material of good corrosion resistance has been increased by improvements in the casting of bronzes of high tin content.[1] These make possible the development of strength comparable with that of steel, combined with soundness and homogeneity that give working properties and corrosion resistance like those long associated with the lower tin bronzes.

The use of bronze to replace steel can often be economic in spite of the increased cost. Thus the replacement of galvanised steel railway signal wire by a bronze wire in corrosive locations, although the initial material cost was higher, had saved two-thirds of the overall cost over a period of forty months.[2]

It is not always realised how much better bronzes can be than brasses, which are so often prone to weakening by dezincification. This is well brought out by tests[3] in which many non-ferrous alloy wires were compared at five test locations; the general superiority of a 6 per cent. tin bronze to many other alloys of good repute is also shown. The losses in breaking strength of some of the wires (mean for all locations) after one year are shown in Table VIII.

TABLE VIII
WEATHERING TESTS OF WIRES

Alloy	*Loss of Strength after One Year per cent.*
6% Tin Bronze..	1·21
H.C. Copper	2·40
3·5 % Aluminium Bronze ..	2·10
70/30 Nickel Copper	3·24
60/40 Brass	18·4
70/30 Brass	8·58

Exposure of sheet as machined tensile test-pieces to American atmospheres[4] over a period of ten years also emphasised, for industrial atmospheres, the superiority of an 8 per cent. tin bronze to 70/30 brass and incidentally showed the striking result of adding 1 per cent. of tin to the 70/30 brass to produce 'Admiralty Metal'. (see Table IX).

Other American tests[5] on screen wire cloth, in which atmospheric exposures were made at several locations, included brasses, aluminium bronze, nickel/copper and a bronze with 2 per cent. tin. Brasses failed rapidly and, after nine years, the tin-bronze showed the least percentage loss of strength at all sites.

The corrosion of bronze in the atmosphere, like that of copper, is usually attended by the formation of a layer of green basic copper salts, mainly sulphate, on the surface. This layer is adherent and protective and can have a pleasant appearance, constituting the so-called patina. The deposit sometimes takes ten to twenty years to reach its best appearance, and sometimes, on statuary, earlier development is desired both for appearance of the metal and to prevent the discoloration of surrounding stone by copper salts. Attention has therefore been given to means of inducing rapid formation of a stable patina[14 15] by treatment with solutions.

TABLE IX
WEATHERING TESTS OF TENSILE TEST PIECES

	Loss of Strength—per cent.—in Ten Years			
	Copper	8% *Tin Bronze*	70/30 *Brass*	*Admiralty Metal* 70 *Cu* 29 *Zn* 1 *Sn*
Altoona (industrial)	5·9	7·2	30·9	9·0
New York (industrial and marine)	6·3	8·0	28·2	7·9
La Jolla (Severe Marine)	7·6	5·7	8·0	2·5
State College, Pa. (rural)	3·1	3·1	3·2	2·2

The corrosion product formed on ancient bronzes that have been buried in the ground usually consists of basic copper carbonate (malachite) with thin layers of oxide (cuprite).[16] The restoration of the form of such material has been successfully carried out by cathodic reduction of the inner layer of the corrosion product.[17] Sometimes, ancient bronzes in a museum develop local deterioration by a recommencement of corrosion, probably due to salts trapped in the surface layers. This, known as 'museum pest' or 'bronze disease' or 'malignant patina', is difficult to prevent. The application of the electrolytic restoration process removes the effect, and usually the cause, but, when the whole article is treated, its appearance is changed. It has been found possible, however, to apply a local electrolytic treatment with good results to the affected spots.[18]

Tin bronzes have also good resistance to corrosion-fatigue. In comparative tests with other copper alloys (containing: 1, aluminium; 2, beryllium; and 3, aluminium, iron and nickel) and stainless steels, a phosphor-bronze with 4 per cent. of tin had a ratio of endurance limit in salt-spray to ultimate stress

of 0·42. This value was equalled only by the more costly beryllium alloy, the next highest value being 0·28.[7] This property assists bronze wire to resist the severe conditions of corrosion, rapid repeated bending and abrasion encountered by fourdrinier wire gauzes in paper manufacture. The substitution of phosphor bronze, with 8 per cent. tin in warp wires and a lower tin content in weft wires, for the 80·20 brass formerly used has been found to increase reliability and life to an extent well worth while. Brass wefts may still be used to ease weaving of the gauze, but a bronze warp is regarded as standard for modern high-speed machines.[22]

The effect of the tin content of bronzes on corrosion during immersion in aqueous solutions is variable, depending, no doubt, on whether the tin can contribute to the formation of a protective layer on the metal surface.

In acids, tin content seems often to have little effect on the total corrosion,[8] but a 5 per cent. tin-bronze lost much less strength than copper (6·7 per cent. against 37 per cent.) when partly immersed in 10 per cent. sulphuric acid, owing to its more uniform corrosion, special attack at the water-line being in particular notably reduced.[9] In hydrochloric acid, bronzes lost more weight than copper in some tests,[9] but less in others,[20] the difference depending on the experimental conditions. Bronzes have very good resistance to phosphoric acid.[8]

In sea-water, alloys of copper with tin were found superior to those with other metals[11] and an increase in tin content up to 10 per cent. produced a progressive improvement.[10] Bronze condenser tubes made from single phase alloy with 10 per cent. of tin have been found in laboratory tests to resist deposit attack, pitting and impingement attack.[6] Bronze compared well with other condenser tube materials of known high quality and has since been found to perform well in service in bad conditions.

An instance has been reported of selective corrosion of phosphor-bronze containing 11–12 per cent. tin,[19] residual copper being left. The material concerned was in the form of cast pump impellers, delivering hot natural water. This appears to be a rare occurrence, possibly associated with porosity of the casting. In laboratory tests,[20] selective removal of tin from bronzes with 12 per cent. or more of tin took place in 1N. sulphuric acid and to a lesser extent in 1N. caustic soda, but not in 1N. hydrochloric acid.

Addition of tin to brasses has long been known to limit their dezincification,[12] probably because it assists the build-up of a protective film, and alloys of the composition: copper, 70 per cent.; zinc, 29 per cent.; tin, 1 per cent. have been used as condenser tubes and in other corrosive environments (see Table IX). The addition of tin to copper-nickel alloys has been found to improve resistance to corrosion by milk, and an alloy with copper, 66 per cent.; nickel, 20 per cent.; zinc, 4 per cent.; tin, 3 per cent.; iron, 2·5 per cent. and manganese, 0·5 per cent. was recommended for dairy plant.[13]

REFERENCES

1. How to Make Improved Chill Cast Tin-Bronzes, Tin Res. Inst. Pub. *TNA*, 1950. For more details see Hanson, D. and Pell-Walpole, W. T., Chill Cast Tin Bronzes, E. Arnold, London, 1951, pp. 78-194.

2. Britton, S. C., J. Inst. Met. (1941) **47**, 119.
3. Hudson, J. C., Trans. Faraday Soc. (1929) **25**, 177.
4. A.S.T.M. Symposium on Exposure Tests for Non-ferrous metals (1946) pp. 29 and 139.
5. Quick, G. W., J. Res. Bur. Standards (1935) **14**, 775.
6. Chapman, J. and Cuthbertson, J. W., J. Soc. Chem. Ind. (1939) **58**, 100, 330. Cuthbertson, J. W., J. Inst. Met. (1946) **72**, 317.
7. Gough, H. J. and Sopwith, D. G., J. Inst. Met. (1937) **60**, 143.
8. McKay, R. J. and Worthington, R., Corrosion Resistance of Metals and Alloys (1936) Reinhold Publ. Corp., New York, p. 439.
9. Bulow, C. L., The Corrosion Handbook, ed. by Uhlig, H. H. (1948), John Wiley & Sons, New York; Chapman & Hall, London, p. 98.
10. Ibid. p. 97.
11. Bulow, C. L., Trans. Electrochem. Soc. (1945) **87**, 127.
12. Bengough, G. D. and May, R., J. Inst. Met. (1924) **32**, 81.
13. Henderson, J. L. and Roadhouse, C. L., J. Dairy Sci. (1940) **23**, 215.
14. Vernon, W. H. J., J. Inst. Met. (1932) **49**, 153.
15. Freeman, J. R. and Kirby, P. H., Metals and Alloys (1934) **5**, 67.
16. Fink, C. G. and Polushkin, E. P., Trans. Amer. Inst. Min. Met. Eng. (1936) **122**, 90.
17. Fink, C. G. and Eldridge, C. H., First Report on the Restoration of Ancient Bronzes and other alloys, New York Metropolitan Museum of Art, 1925.
18. Evans, U. R., Chem. and Ind. (1951) p. 710.
19. Clark, W. D., J. Inst. Met. (1947) **73**, 263; discussion, p. 763.
20. Bauer, O., Vollenbruck, O. and Schikorr, G., Mitt. Mat. Pruf. Anstalt (1932), Sonderheft **19**, 3.
21. Dillie, D. C., Metals and Alloys (1940) **11**, 50, 77.
22. Anon., Met. Ind. (London) (1939) **54**, 627.

ADDITIONAL BIBLIOGRAPHY

General summaries of information on corrosion of bronze:

McKay, R. J. and Worthington, R., Corrosion Resistance of Metals and Alloys, Reinhold Pub. Corp., New York, 1936, pp. 432–455.

Bulow, C. L., The Corrosion Handbook, Ed. Uhlig, H. H., J. Wiley & Sons, New York, 1948, pp. 96–103.

Hanson, D. and Pell-Walpole, W. T., Chill Cast Tin Bronzes, E. Arnold, London, 1951, p. 254.

Corrosion of ancient bronzes:

Collins, W. L., J. Inst. Met. (1931) **45**, 23.

Elam, C. F., J. Inst. Met. (1932) **48**, 589.

Part III

COATINGS OF TIN AND TIN ALLOYS

TIN COATINGS ON IRON AND STEEL—METHODS OF APPLICATION AND GENERAL PROPERTIES

Because of its corrosion resistance, non-toxicity, solderability and attractive appearance, tin is widely used as a coating on iron and steel products. The greater part of this use relates to steel tinned in sheet form to produce tinplate for the subsequent preparation of a great diversity of articles, but many ferrous products are tinned when their manufacture is at or near completion. Full information is readily available elsewhere[1 2 3 4] about the methods of application and physical characteristics of tin coatings, and only a brief summary of essentials need be given here.

Methods of application

HOT-DIPPING. The most widely-used method of coating steel with tin is by dipping the metal into molten tin. The pickled steel is first dipped in flux or in a grease-pot, then into one or a series of pots of molten tin, and finally drained in air or in a grease-pot. This general method is applicable to all ferrous materials, but cast iron requires special methods of pre-cleaning and some steels may also require special pickling.

In the production of the common grades of tinplate, the operation is mechanised and the coated sheet emerges from the molten tin into a bath of palm oil, passing through rolls which remove some tin to leave a coating of thickness 0·06–0·1 mil. Without wiping, the coatings produced by hot-dipping are commonly 0·5–1 mil. thick, but coatings up to 3 mil. thick can be attained.

During hot-dipping, some alloying between tin and iron occurs and an inner layer of the coating, 0·01–0·02 mil. thick, is in the form of tin-iron compound.

ELECTRODEPOSITION. Tinning by electrodeposition is now well established. The rate of deposition possible and the quality of the deposits obtained have been much improved by many developments in the last twenty years. The constitution of the baths used is described in another publication.[4]

The high rates of deposition from the newer baths have permitted the electrolytic method to be used in the production of tinplate as continuous strip and, in the U.S.A., production by this method now exceeds that by

hot-dipping. Electrodeposition permits better control of thickness than hot-dipping and allows the application of thinner coatings (down to 0·015 mil.) which are considered adequate for containers of dry non-corrosive material (p. 60).

The electrodeposits on sheet are commonly flash-melted after the deposition to produce a bright surface and then receive a passivating treatment and an oil dressing. Electrodeposits on other material are usually left as deposited.

CHEMICAL REPLACEMENT.[10] Very thin tin coatings may be applied to small articles such as pins by tumbling them in a suitable electrolyte with zinc which supplies a sufficient current without an external source. In one method the articles are immersed with zinc in a hot solution of stannous chloride, cream of tartar and ammonium alum. Immersion in fused salts, e.g. stannous chloride, can also produce thin deposits.[11] A method of plating from an alkaline sodium stannate bath without using applied current has been found capable of producing deposits up to 2 mil. thick with properties as good as those of normal electrodeposits.[12] The work is coupled to aluminium immersed in the solution and tin is deposited at the rate of about 0·2 mil. per hour.

SPRAYING. Tin can be sprayed by any of the commercial methods and application in this form is suitable when large coating thicknesses are required, e.g. in food industries.

WIPING. Tin coatings can be applied by a wiping technique, when other methods are unsuitable. The surface to be coated is covered by flux and heated above the melting point of tin. Tin is then wiped on to the surface. Alternatively, the tin and flux may be applied together as a 'tinning paste', the tin in powder form being suspended in a flux solution. The paste is brushed on to the surface which is then heated and wiped.

Coating thickness terminology

The coating thickness on tinned sheet is commonly expressed in the U.K. as pounds or ounces per basis box (base box in U.S.A.). The basis box is a unit of area equivalent to 56 sheets each 28×20 inches, i.e. 31,360 sq. in. of sheet; 1 lb. of tin per basis box is equivalent to a coating thickness of 0·0606 mil. The whole system of grading and nomenclature has been conveniently summarised in another publication.[5] The choice of coating weight for particular applications is dealt with later (p. 61).

Porosity of coatings

Coatings produced by any of the methods may contain pores penetrating to the steel. Means of estimating the number of pores are mentioned later (p. 62).

The porosity of hot-dipped coatings depends on the thickness according to a logarithmic relation.[6] The number of pores is insignificant at a coating thickness of 0·3 mil., but may be 2,000–3,000 per sq. dm. at the common tinplate thickness of 0·09 mil. Even so, the area of steel exposed on the 0·09 mil. coating has been estimated at only 0·67 sq. mm. per sq. m.[7]

For coatings electrodeposited from an acid sulphate bath or from a sodium

stannate bath the number of pores was found to vary inversely with the square of the thickness.[8]

The relations between porosity and thickness quoted refer to sheet in its original condition. Deformation has the effect of increasing porosity[9] owing to the opening of 'concealed' pores which are bridged over in the undeformed sheet. This effect is frequently of great importance since sharp bending is involved in the formation of seams of tinplate containers.

Although the area of steel exposed at pores is very small, it enters very largely into the corrosion behaviour and, although the corrosion of the thicker, almost pore-free, deposits is effectively the corrosion of tin, the thinner coatings such as those of tinplate require special consideration.

REFERENCES

1. Hoare, W. E. and Hedges, E. S., Tinplate, Ed. Arnold & Co., London, 1945.
2. Hoare, W. E., Hot-Tinning, Tin Res. Inst. Pub. TOI, 1948.
3. Hoare, W. E., J. Inst. Prod. Eng. (1951) **30**, 104. (Account of electrolytic tin-plate processes.)
4. Instructions for Electrodepositing Tin, Tin Res. Inst. Pub. HI, 1949.
5. Hoare, W. E., Tinplate Handbook, Tin Res. Inst. Pub. TCT, 1950.
6. Hoare, W. E., J. Iron and Steel Inst. (1937) **136**, 99.
7. Hoare, W. E., Phil. Mag. (1938) **26**, 1077.
8. Caulfield, K. W., Kerr, R. and Angles, R. M., J. Soc. Chem. Ind. (1947) **66**, 5.
9. Macnaughtan, D. J. and Prytherch, J. C., J. Electrodep. Tech. Soc. (1937) **12**, 65.
10. Mantell, C. L., Tin, Reinhold Pub. Corp., New York, 2nd Edition, 1949, p. 194. (This describes some of the processes. A list of solutions used may be obtained from the Tin Research Institute.)
11. Hoge, H. R., Metal Progress (1947) **52**, 819.
12. Wilson, J. K. and Wright, O., Electroplating (1951) **4**, 274.

TIN COATINGS ON STEEL IN THE ATMOSPHERE

Tin is usually considered to be cathodic to steel in exposure to the weather, but exposure in different localities in U.S.A. of discs of tin and steel coupled together suggested that, in marine atmospheres, tin could be anodic to steel and, in industrial atmospheres, was cathodic[1]. It appears, however, that any anodic relation of tin to steel is never sufficient to give complete protection to steel exposed at pores in a tin coating, for, in all atmospheres, some rust quickly appears at pore sites. Contrary to the findings with coupled discs, rusting at pores is much more restrained in smoke-polluted atmospheres

than it is by the sea or in rural locations. On exposure to urban and suburban atmospheres, electroplated tin coatings, 0·3–1·0 mil. thick, permitted the early appearance of rust, but this disappeared and active rusting was delayed as long as it was by zinc coatings of similar thickness.[2] By the sea, rusting at spots continued uninterrupted. Electrodeposited tin coatings, 3 mil. thick, were still giving good protection, apart from a few rust spots, after five years in another industrial atmosphere, but rusting spread much more rapidly in a seaside atmosphere, covering 5 per cent. of the area in 1·5 years, and at a wet rural location, covering 5 per cent. of the area in 2·8–3·6 years.[3]

Provided that the conditions allow frequent drying out, so that the rust forms hard plugs in the pores, it is doubtful if the penetration of the steel is ever accelerated by a tin coating in atmospheric corrosion. If the coating be sufficiently thick the steel can be well protected. Thus, in intermittent salt spray, an electrodeposited tin coating 0·5 mil. thick allowed rust staining to appear at once, but by the time that a bare steel plate of 14 S.W.G. was perforated and a zinc-coated plate severely rusted, the points of corrosion in the steel base of the tin-coated plate were still barely perceptible when the coating was removed.[2] With thin coatings, in the common tin-plate range, this checking of corrosion at the pores does not so readily occur, since the resistance of the corrosion cell between tin surface and pore bottom is less for the smaller coating thickness. In full exposure to the weather, the pores grow by undermining the surrounding coating, and in due course the whole surface rusts.

Tinplate usually carries enough residual grease from the manufacturing process to give protection to the pores for a short time in mild moisture condensation. In long storage with intermittent condensation some rust may appear, and although the loss of appearance is undesirable, only in exceptionally adverse conditions is there danger of perforation.

If the surface is wet for long periods, e.g. by collection of a pool of rain or spray or by condensation, the loose rust formed does not assist checking of electrolytic action at pores. Perforation of tinplate then becomes a possibility and disfigurement is certain. A moist environment that may be enduring can be produced by labels fixed to tinplate containers, and even wrapping paper can inflict injury if it becomes damp, especially with saline moisture, as is always possible in sea-transport.

Since even disfigurement by rust is undesirable, much attention has been given to means of packing, storage and transport of tinplate sheets and containers.

A list[4] of factors leading to rusting of sealed cans included:

1. Bad storage conditions which permit condensation.
2. Splashing of the containers during filling, especially if the contents are in brine.
3. Exhaust box temperature too low. It should be above 205° F.
4. Marking devices which break the coating.
5. Unsuitable cooling water.

6. Packing cases containing too high (more than about 16 per cent.) a content of water.

7. Hygroscopic label pastes.

Stacking cans on ends may be worse than stacking on sides because it aids water collection.[5] Rusting of tins packed in wooden cases was found[6] to be severe if the wood had a moisture content above 17 per cent., but to decline to slight amounts as the moisture fell below 14 per cent. Lumber dried in summer had a moisture content of 12–14 per cent., but, if dried in winter, the content was rarely below 20 per cent., and was thus above the limit of safety. Western Hemlock and Sitka Spruce were found to give similar results. Dust may promote rusting in condensation conditions.[14]

Tests of wrapping paper enclosing bundles of tinplate showed that the use of water-repellent paper would not prevent losses in severe condensation, but a waterproof paper could keep losses low if properly sealed and free from tears. A metal wrap was found to be inadequate if the overlaps were too small or if a waterproof paper was not also used. Papers impregnated with a vapour-phase inhibitor were disappointing. Some promise has, however, been obtained by the use of papers impregnated with 5 per cent. sodium benzoate,[8] provided that the paper contains less than 0·1 per cent. chlorine (as chloride). The use of cyclohexamine carbonate as a vapour-phase inhibitor also seems promising.[9] A chloride content of less than 0·1 per cent. in wrapping paper seems generally desirable.[10]

Unsuitable cooling waters used after processing filled cans may cause immediate corrosion. A chloride content in the water exceeding 150 parts per million may be expected to give trouble.[11] Treatment of the water by alkalis is sometimes useful in checking the rusting tendency, but care has to be taken not to add sufficient to etch the tin and not to add too little and cause intensified pitting. Control of the pH in the range 9–9·5 has been recommended[11] as a general guide, but experiment for each water supply is desirable. This also holds good for the additions of chromate which have also been recommended.

When prolonged storage in adverse environments has to be endured, lacquering of the outside of cans is useful,[12] but is not possible for all tin-coated products. It is also possible to check rusting at pores by chemical treatments. The Protecta-Tin process[13] referred to earlier as a means of preventing staining of tin by sulphur compounds (p. 28) also confers a degree of rust resistance which will endure for many weeks of full weathering. The solution now used contains 10 g. caustic soda, 3 g. sodium dichromate and a small amount of wetting agent in 1 litre of water. It is used at a temperature of 85–95° C. and the work to be treated is immersed in it for a brief period whose minimum length for best results depends on the heat capacity of the work and the greasiness of its surface. A 3-seconds immersion has given good results in the treatment of tin-plate sheets or empty cans. The process will not prevent rust if the surface is submerged for long periods in pools of water, but is very suitable as a counter to most bad storage conditions.

Immersion in a solution containing 10 g. chromic acid and 50 ml. phosphoric acid at 85° has been found to give even better protection against rust than the Protecta-Tin process. However, a longer period of immersion is required and the condition of the metal is important. A hot-dipped coating requires to be cathodically cleaned beforehand and an electrodeposited coating also requires this if not freshly applied. This process seems more suited, therefore, to treatment of electrodeposited tin for such applications as electrical apparatus than to treatment of tinplate.

Usually, electrolytic tinplate is given a passivating dip in a solution with or without applied current. The solutions used are acid or alkaline chromate and/or phosphate solutions which would be expected to give some degree of protection against rusting.

REFERENCES

1. Reports of Subcommittee VIII on Galvanic and Electrolytic Corrosion, Proc. A.S.T.M. (1935) **35** (1), 167; (1939) **39** (1), 296.
2. Britton, S. C. and Angles, R. M., Metallurgia (1951) **44**, 185.
3. Hudson, J. C. and Banfield, T. A., J. Iron & Steel Inst. (1946) **154**, 229P.
4. 'The External Rusting of Food Cans,' American Can Co., 1933.
5. Rep. of Canadian Govt. Forest Prod. Lab.,—Australian Food Manufacture (1946) **16**, 24.
6. Reps. of Research Committee on Marine Moisture Damage, Ass. of Marine Underwriters of British Columbia, Bull. No. 8, Sept., 1939.
7. Wellinger, D. H., Am. Iron & Steel Inst. Year-book (1950) 442.
8. Ann. Rep. of Chem. Res. Board, D.S.I.R., London (1948) p. 16.
9. Ibid. (1949) p. 22.
10. British Standard Spec. 1133, British Standard Packaging Code (1943) p. 717.
11. Dykstra, K. G., Sheet Metal Ind. (1940) 14, 839.
12. Smith, H. R., Proc. Inst. Food Tech. (1944) 26.
13. Anti-rust and Anti-staining Treatment for Tin-plate (The Protecta-Tin Process), Tin Research Inst., Pub. TCN, 1950.
14. Sanders, R. K., Chem. Ind. (1949) 151.

TINNED STEEL CONTAINERS FOR ACID PRODUCTS

In some acid solutions, tin is anodic to steel (p. 17) and contact of the two metals accelerates the corrosion of tin but retards that of steel. It seems likely that, in all acids, tin is anodic to steel temporarily when the oxide films on the surfaces are first dissolved,[3] but this may only be a momentary effect. The persistence of anodic behaviour depends on the depression of the tin ion

concentration in the solution by the formation of complex tin compounds. This is governed by the nature of the acid, its concentration and the presence of other materials capable of removing tin ions. Persistent anodic behaviour was observed in citric and oxalic acids[1 3] and in sulphuric and hydrochloric acids with pH below 1.[1] In malic acid of 0·75 per cent. concentration (corresponding to apple juice acidity) there was little mutual effect, and in solutions of equivalent acidity made with acetic, malonic and succinnic acids tin was the cathodic member of the couple.[1] In hydrochloric and sulphuric acids with pH above 1, tin was also cathodic. The addition of other substances which could remove tin ions tends to make tin anodic in all acid solutions. Apple pomace and fruit seeds contributed such materials.[1]

Fruits and many vegetables contain citric, oxalic or other acids and other substances capable of forming complexes with tin ions. Consequently, inside a sealed tinplate can of such products, steel exposed at pores in the coating is usually cathodic to tin. The electro-chemical effects resulting may be insufficient to ensure that the steel is immune from corrosion, but at least they prevent a concentration of the attack on pores in the coating which could lead to rapid perforation. Moreover, the stannous ions remaining free have independently a substantial inhibitive effect on the corrosion of steel,[1 2 3] an effect possibly due to their removal of sulphur compounds.[4] The amount of tin required to reduce the corrosion of steel is extremely small, and the addition of two parts of tin per million halved the corrosion rate in 0·5 per cent. citric acid.[21]

The air supply in a sealed container is, of course, very limited, so that the progress of corrosion is mainly dependent on the evolution of hydrogen as gas. Thus, if the surface were unbroken tin, corrosion would be extremely slow, but the exposed iron is able to discharge hydrogen and this, in addition to permitting more rapid corrosion, introduces another difficulty. The hydrogen in time may distend the can. The swollen can, termed a 'Hydrogen swell' or 'Springer', is indistinguishable to the intending purchaser from a can swollen by decomposition of the contents and is thus unsaleable. It is therefore necessary, in addition to preventing the local action leading to perforation, to keep all corrosion to the lowest possible level.

A number of substances have been found to act as corrosion inhibitors. Sugar is one[5] and a constituent of unrefined beet-sugar is particularly active.[6] Gelatin and various colloidal materials also act as restrainers. On the whole they tend to be more effective in the more acid products, an effect ascribed to the tendency of the colloid particles to migrate to the cathode at pH values lower than that at their iso-electric point.[7] Probably for this reason, less acid fruits such as prunes, cherries and bilberries are more liable to produce hydrogen swells than are more acid fruits such as gooseberries. It is indeed worth while to add acid to some fruits.[8 9 10] Most of the inhibitive substances are naturally present in canned fruit and in practice little has been achieved by deliberate additions of such materials. Some success has been claimed for the addition of an inhibitor such as thiourea by incorporating it in the sealing medium in the can end.[11] The results apparently depend on the pack: for

beets, an improvement in service life was found, but for tomatoes there was no significant effect.[12]

Some substances can accelerate corrosion, e.g. oxygen, oxidising agents and sulphur. When they cannot be excluded, special measures to protect the can such as lacquering, referred to later, may be taken.

The effect of traces of residual oxygen in a can may be serious, but the need for the fullest possible exhaustion is well appreciated. Some oxidising materials, however, can also act as depolarisers. These include the anthocyanin pigments,[13] naturally present in many fruits, and nitrates.

Sulphur compounds, whether of organic or inorganic origin, have special effects. At low acidities, as in meat and many vegetables, these may produce unsightly staining. This is referred to later (p. 54). In the acid products they influence the corrosion of both tin and steel, but the nett effect is variable.[14] In more acid products with a pH below 4, the potential of steel is depressed and the metal may become anodic to tin. The rate of corrosion of the steel is increased and an increased liability to perforation results. In less acid media, the corrosion of both tin and steel may be retarded. Canning trials have shown that sulphur compounds derived from fruit-spray residues increased the proportion of hydrogen swells with gooseberries, but reduced troubles with the less acid cherries.[15] The addition of small amounts of sulphur, as thiosulphate, has actually been advocated for the less acid products, but, for the general run of fruits, it is considered desirable to avoid even the small quantities of sulphur introduced in the ultramarine used in 'blueing' sugar or in fruit-spray residues.

The temperature of storage has a pronounced effect on the incidence of 'hydrogen swells' and perforations, a rise of even from 50° F. to 70° F. producing a substantial deterioration.[20]

The nature of the steel-base used for the tinplate is of great importance, but unfortunately the requirements for the best results depend somewhat on the fruit. A great deal of experimental work has been carried out; much of it concerned pack-rolled steel, and the results obtained may not be applicable to cold-reduced strip, but many results are not in doubt. The progress of the investigation of this matter has been well summarised elsewhere,[16] and only the main results need be mentioned.

The phosphorus content should be low, and in U.S.A. a special grade of steel with 0·015 per cent. max. is produced. The copper content has variable effects, increase in this element being bad for cherries or prunes, but good for loganberries and gooseberries. No doubt the effect of the steel is produced by the number of points on its surface which are specially active in catalysing the evolution of hydrogen, and the efficiency of such points depends on what is absorbed on them from the contents of the can.

Fruit cans are often lacquered internally. The original object of this was to present a bright unetched surface to the consumer, and to prevent the discoloration which is brought about by the action of tin salts on some fruits. More recently, lacquering has been used as a tin conservation measure to

give protection to thinly-coated sheet from the electrolytic tinning lines which may not have a coating thick enough to provide for a long storage.

Although lacquering achieves its object of preserving a more attractive interior, it has been known to increase the incidence of hydrogen swells.[17] If defects in the lacquer and defects in the tin coating were independent, all would be well, but the tendency is for them to occur together, particularly in seams. Thus, in the lacquered can the ratio of exposed tin surface to exposed steel surface may be much reduced with a consequent diminution in the protection of the steel by the anodic tin surface or by stannous ions. The possibility that, in some packs, the lacquered surface may act as a cathode to the bare surface exposed at breaks in the lacquer also exists. Such an occurrence has been shown to take place in salt solutions,[18] probably owing to the differential rates of penetration of lacquer films by anions and cations.[19]

It is now well appreciated that, if lacquering is worth doing, it is worth doing well. Double-lacquering of sheets and the addition of a strip of lacquer down the seams of finished cans are practised for troublesome packs. With the proper precautions taken, lacquering provides a good means of reducing corrosion and of retaining a good appearance of products and of container.

Containers which have some air between contents and closure or whose contents are only slowly consumed after opening may be rust-spotted on their air-exposed surface. Even when the bulk contents are such as to be innocuous to tinplate, the vapours arising from them may not carry substances favouring anodic behaviour of tin. Moreover, the complete protection of the steel is never to be expected and, in exposure to the air, any action on the steel produces visible rust. Lacquering will prevent this action.

Acid products, such as fruit juices and preparations made with them, in which tin is anodic to steel, may be handled in tinned steel vessels open to the air. Although, in these conditions, the loss of tin is at a greater rate than it is in the sealed can, it is still slow. A heavy tin coating is applied and its gradual wastage is accepted as producing a less undesirable contamination of the product than would result from the use of other materials of comparable cost. The vessels are in due course re-tinned. Acid solutions, such as those containing mineral acids in which tin is cathodic to steel, are not in general suited to handling in tinned steel. In concentrations of mineral acid producing anodic behaviour of tin, the rate of removal of tin is too high.

REFERENCES

1. Kohman, E. F. and Sanborn, N. H., Ind. Eng. Chem. (1928) **20**, 1373.
2. Lueck, R. H. and Blair, H. T., Trans. Am. Electrochem. Soc. (1928) **54**, 257.
3. Hoar, T. P., Trans. Faraday Soc. (1934) **30**, 472.
4. Hoar, T. P. and Havenhand, D., J. Iron and Steel Inst. (1936) **133**, 253P.
5. Morris, T. N., Ann. Reps. Food Investigation Board, D.S.I.R. (1929), p. 82; (1930), p. 119; (1931), p. 191.
6. Morris, T. N., Ann. Rep. Food Investigation Board, D.S.I.R., (1934), p. 183.

7. Burns, R. M. and Schuh, A. E., Protective Coatings for Metals, (1939), Reinhold Pub. Corp., New York, p. 158.
8. Morris, T. N. and Bryan, J. M., D.S.I.R. Food Investigation, Special Report No. 40 (1931), p. 73.
9. Hirst, F. W. and Adam, W. B., Univ. Bristol Res. Station, Canning Bull. No. 1, 1930.
10. Kohman, E. F. and Sanborn, N. H., Ind. Eng. Chem. (1930) **22**, 615.
11. Stevenson, A. E. and Flugge, S. L., U.S. Patent 2,168,101.
12. Brighton, K. W., Trans. Electrochem. Soc. (1943) **84**, 227.
13. Kohman, E. F., Ind. Eng. Chem. (1924) **16**, 290.
14. Morris, T. N. and Bryan, J. M., D.S.I.R. Food Investigation Board, Special Report No. 40 (1931), p. 63.
15. Clough, R. W., Shostrom, O. E. and Clark, E. D., Canning Age, (1924) **5**, 531; (1930) **11**, 402.
16. Hoare, W. E. and Hedges, E. S., Tinplate (1945), Ed. Arnold & Co. Ltd., London, p. 239.
17. Kohman, E. F., Food Manuf. (1929) **4**, 292.
18. Crennell, J. T., J. Soc. Chem. Ind. (1950) **69**, S36 and 371.
19. Mayne, J. E. O., J. Oil and Colour Chem. Ass. (1949) **32**, 481.
20. Kohman, E. F., Nat. Cann. Ass. U.S.A. Bull. No. 23L (1927).
21. Morris, T. N. and Bryan, J. M., Trans. Faraday Soc. (1933) **29**, 395.

ADDITIONAL BIBLIOGRAPHY

Pick-up of metal by canned foodstuffs:

Morris, T. N. and Bryan, J. M., D.S.I.R. Food Inv. Board, Special Rep. No. 40 (1931).

Adam, W. B. and Horner, G., J. Soc. Chem. Ind. (1937) **56**, 329T.

Lynch, L. J. and Kefford, J. F., J. Council Sci. Ind. Res. Australia (1939) **12**, 303.

Summary of canning experience with Foodstuffs (need for lacquer, etc.):

Mantell, C. L., Tin, Reinhold Pub. Corp., New York, 2nd Edition, 1949, pp. 499 and 502.

Production and Lacquering of cans:

Farrow, F. D. and Green, T. G., Chem. Ind. (1941) **19**, 95.

TINNED STEEL CONTAINERS FOR PRODUCTS OF LOW ACIDITY

In canned foodstuffs other than fruit, the limited air supply keeps corrosion of the oxygen-absorption type to a slow speed and the acidity is often too low for rapid hydrogen evolution. Some vegetables may contain oxidising agents, such as the anthocyanin pigments or nitrates, or may be sufficiently

acid to promote hydrogen evolution without being acid enough for the colloidal corrosion restrainers to be effective. Spinach and beetroot are examples of vegetables that may corrode tinplate. Since adjustment of the pH value or other additions cannot be made without interference with flavour, lacquering is the only safeguard.

In some meats, vegetables and marine products, sulphur compounds may give rise to staining of the tin surface and, in severe cases, to the production of black iron sulphide at discontinuities in the coating. The action of sulphur compounds on tin has already been mentioned (p. 28), when it was pointed out that the amount of metal removed was small, the objection to it being the production of unsightly stains.

It is, however, desirable that the staining be prevented and the formation of iron sulphide, which may discolour the contents of a can, is particularly to be avoided. Investigations of the effect of treatment of the product have shown that, for marine products such as lobsters, the discoloration is affected by the season of capture and increases with the interval between capture and canning[1] and that, for corn, staining increases with the maturity of the produce canned and with time and temperature of cooking.[2] Iron sulphide is not deposited if the pH value is below 6·5.[3]

Complete protection against staining of the tin coating may be achieved by treatment of the can. Zinc oxide is able to absorb the sulphur compounds without change of colour[4] and lacquers pigmented with this compound have been used with success to provide an unstained, although white, container. Treatment of the tinplate in a chemical solution is an attractive alternative. The 'Protecta-Tin' process (pp. 28 and 48) has been found very effective for soups, meats, vegetables and marine products.[5, 6] In conditions favourable to the production of iron sulphide, fracture of the tin coating after treatment, as for example in sealing the can, may prevent the complete success of either lacquering or chemical treatment.

Some marine products contain amines which may attack tin. For shrimps, the methylamine that appears to be injurious is said to be largely removed if the produce is allowed to lie on ice for a day or two before packing.[7]

In most natural or domestic supply waters and in distilled water, tin behaves cathodically to steel. In hot water, cathodic action starts immediately after immersion, but in cold water, a preliminary phase has been observed to last for some hours during which tin appeared to act anodically.[16] Corrosion at the pores of sealed tinplate containers of water prepared for military supplies may be sufficient to affect flavour. Lacquering or wax-coating of such cans has, therefore, been recommended.[12] Open tinned steel containers may, however, be used satisfactorily with many waters, even hot water, for short periods of contact, e.g. urns and kettles. The success of this use appears to depend on protection of the pores by scale deposited from the water and, in soft waters where this is not possible, the use of tinned steel is not practicable. For any water supply, a tin coating of good quality, with a low pore count, is desirable to ensure long life, and harsh cleaning treatments which remove all scale, and possibly some tin, should be avoided.

Many aqueous preparations are handled and marketed in tinplate containers, e.g. milk, cattle-dips, many food products, insecticides and phenolic disinfectants, without even disfigurement of the metal. The tin coating resists a wide range of products, but, to prevent corrosion at pores, it is desirable that strong electrolytes such as chlorides or sulphates should not be present in substantial amounts and that the product should be slightly alkaline, i.e. with a pH of 8–9. Products, slightly acidic by nature, as phenol, or by the presence of impurity, as formalin, may produce some attack of tin or of steel depending on the nature of the acid, which may at least mar the appearance of the container or the product. In some instances, however, high viscosity, which restrains oxygen diffusion, or the presence of corrosive-inhibitive substances may keep corrosion to an insignificant level, and it is often not possible without trial to predict whether any material is unsuited to handling in tinned steel. Lacquering or wax-coating may be used as a safeguard, especially in those instances where contamination of a product is feared, e.g. beer (p. 19).

The more alkaline materials, with pH above 10, may etch the tin coating, but, in contact with them, steel is cathodic to tin and the soundness of the container is not threatened. Hydrogen may be evolved, but not so readily as in acids, and a large steel area needs to be exposed before any risk of can distention appears.[8] The use of containers with untinned ends seems, however, to be inadvisable. Many alkaline cements and cleaning materials are packed in tinplate containers, with no visible effects other than etching of the coating.

Many non-aqueous liquids such as organic solvents, oils and petroleum products are without effect on tinplate and may be stored or used in tinplate containers. For products immiscible with water, there is a slight risk in conditions of use that may permit access of water, e.g. petrol tanks. A small amount alighting on an area of exposed steel may corrode it seriously, the steel in such a case being anodic to the tin coating. For products which may be adversely affected by very small amounts of metallic contamination, the container may be coated with lacquer or wax. Some polishes and varnishes for wood may give dark results if they contain iron, but the addition of corrosion inhibitors is possible and good results have been reported for the addition of small amounts of aromatic amine phosphates to french polish and to shellac.[10, 11]

Dry goods, coffee, cocoa, mustard, etc., are without effect, the requirement of the tin coating for these being that it shall remain bright and shall prevent external rust in reasonable storage conditions. The slight condensation which may be expected from less dry materials, such as tobacco, is taken care of by the residual grease in the pores. Dry materials containing inorganic salts such as photographic chemicals, dyestuffs, fertilisers and insecticides, especially if also containing hygroscopic substances, may produce disfigurement unless really dry and completely filling a container with a well-fitting closure.

The corrosion of tinplate used in the construction of gas-meters has had

some attention,[13 14] although, with a heavily-coated plate, satisfactory service is usually given. Laboratory experiments[9] using water saturated with coal gas with and without additions of ammonia and hydrogen sulphide suggested that the presence of ammonia was responsible for intensified rusting at pores. The lacquering of the inner surface and adequate painting of the outer surface has been recommended as a safeguard.[15]

REFERENCES

1. Harrison, F. C. and Hood, E. G., Hon. Advis. Coun. Sci. Ind. Res. Ottawa, Rep. No. 12, 1923.
2. Fitzgerald, F. F., Bohart, G. S. and Kohman, E. F., Nat. Can. Ass. U.S.A. Bull. No. 181, 1922.
3. Dill, D. B. and Clark, P. B., Ind. Eng. Chem. (1926) **18**, 560.
4. Bohart, G. S., Nat. Cann. Ass. U.S.A. Circ. No. 101, 1924.
5. Kerr, R., J. Soc. Chem. Ind. (1940) **59**, 259.
6. Kefford, J. F. and Lynch, L. J., J. Coun. Sci. Ind. Res. Australia (1941) **14**, 16.
7. Bigelow, W. D. and Bacon, R. F., Ind. Eng. Chem. (1911) **3**, 832.
8. Britton, S. C., J. App. Chem. (1951) **1**, S 132.
9. Jones, S. and Speers, J. A., Gas World (1948) **128**, 520.
10. Sanders, R. K., Chem. Ind. (1947) 151.
11. Drown, W. E., Oil, Paint, Drug Reporter (1951) **159**, 74.
12. Mutschler, M. J., Food Ind. (1946) 83.
13. Lessing, R. J., Gas Lighting (1916) **134**, 586.
14. Trans. Inst. Gas Eng. (1917) 142.
15. Nairne, C. L., Gas Age Rec. (1934) **34**, 172.
16. Macnaughtan, D. J., Clarke, S. G. and Prytherch, J. C., J. Iron and Steel Inst. (1932) **125**, 159.

TIN COATINGS ON STEEL AS A PREPARATION FOR PAINTING

The bright durable surface of tinplate has long been exploited as an excellent base for the production of coloured decoration and means have been developed for printing decorative and labelling designs on containers for biscuits, sweets, polishes and many other materials in very large numbers.[6 7] The coatings applicable by these means have usually not a high protective value, but they have a long life indoors as the tin coating prevents corrosion developing beneath them. Paints designed to protect steel against the weather can also be helped very considerably to prevent rust by tinning the metal before they are applied.[1 2]

It has already been pointed out that the development of rust on unpainted

tinned steel is slow in spite of early appearance of rust at pores (p. 46). The additional protection of a paint coating stops even this initial action, and rusting is delayed until the paint is substantially decayed by its own ageing changes. The painted tin does not show cathodic behaviour to steel exposed at a scratch and, even in salt spray, there is much less spread of damage to surrounding paint with a tinned surface than with an untreated one.[4] A cathodic action round the scratch would produce alkali with a destructive effect on paint adjesion.

A thin coating only is needed to produce appreciable benefit. A tin thickness of 0·05 mil. gives results comparable with those produced by the phosphate treatments that are widely used as a preparation for painting, both in preventing the appearance of rust on an unbroken paint coating and in delaying spread of rust from a scratch or other discontinuity in the paint.[3, 4] The very thin tin coatings produced in the Bullard-Dunn pickling process (p. 44) have been shown to give considerable assistance to the protection obtained by painting[5], although better results are obtained if the deposit is reinforced by the deposition of a little more tin.

Tin is inert to paints and there appears to be no need to fear loss of adhesion by interaction of the metal with any paint materials. Adhesion, i.e. resistance to the removal of paint by physical damage as distinct from corrosion, is, however, affected by the type of tin surface used. Electrodeposits of tin from the alkaline sodium stannate bath are sufficiently matte to give a good 'key' for paint[4] and are preferred as the means of preparation for painting. The surfaces of hot-dipped and wiped coatings and of flash-melted electrodeposits are smooth and require paints with good adhesive properties when liability to physical damage is feared. Moreover, hot-dipped coatings may carry grease residues on their surface. These residues may contain tin soaps that are rather resistant to removal by solvent degreasing and, when paints intolerant of them have to be used, alkaline degreasing is useful. A very effective cleaning method that leaves the metal surface bright is cathodic treatment in 0·5 per cent. sodium carbonate solution, cold, with 4–6 volts between the work and steel or nickel anodes. After alkaline cleaning in any form, thorough rinsing and drying should, of course, be carried out before painting. When the work cannot be immersed, swabbing with a mixture of 5 parts of concentrated hydrochloric acid and 95 parts of industrial alcohol, until the tin is visibly etched, provides an improved surface for painting.

It is often impracticable to apply a tin coating to the whole of a finished steel product before it is painted. The spread of rust under the paint from edges or other parts specially susceptible to early breakdown can, however, be prevented by the local application of tin or solder coatings by wiping.[2] A 'tinning paste' (p. 45) is brushed on, heat is applied and the coating is wiped on with a cloth. This method has been found suitable for the treatment of window and door edges of automobile bodies.

For painted steel immersed in water, a tin undercoat considerably reduces blistering of the paint and the spread of rust, but, especially in salt water,

there may be accelerated penetration of the steel if it becomes exposed by scratches or other physical damage.

REFERENCES

1. Hedges, E. S. and Jordan, L. A., J. Iron and Steel Inst. (1945) **152**, 429P.
2. Britton, S. C., J. Oil and Colour Chem. Ass. (1950) **33**, 120.
3. Britton, S. C., Sheet Metal Ind. (1948) **25**, 1185.
4. Britton, S. C. and Angles, R. M., J. Iron and Steel Inst. (1951), **168**, 358.
5. Kronsbein, J., J. Electrodep. Tech. Soc. (1940) **16**, 55.
6. Matthison, A. Ll., Tinplate Decoration and Lacquering of Food Containers, A. Holden & Sons Ltd., Birmingham, 1931.
7. Hoare, W. E., The Decoration of Tinplate by Printing and Varnishing, Tin Res. Inst. Pub. B.4, 1937.

SPECIAL APPLICATIONS OF TIN COATINGS ON IRON AND STEEL

Tinning of iron and steel is carried out for several purposes not directly connected with corrosion, e.g. to provide a sealing surface in a joint or to facilitate soldering. Even in these instances, the protection may be useful and in the case of soldering, the use of a milder flux made possible by the use of a tinned surface may avoid corrosion troubles. In addition, there are applications of tin coatings for resistance to special forms of corrosion.

In 1931, the tinning of cast iron pistons for motor vehicles was found to be of great benefit in reducing piston and cylinder wear, and was later extended to piston rings and to the pistons of aircraft and other internal combustion engines. The coating, which is applied by electrodeposition,[1] may be as little as 0·2–0·3 mil. thick, but thicknesses up to 0·6 mil. are used.

The function of the tin coating is to facilitate bedding down of the rubbing surfaces during the running-in period. The tin acts as an adjustable gasket between rings and bores, provides some metallic lubrication and resists acid corrosion. Scoring and scuffing are therefore very much reduced.[2 3] Tin coatings appear to be superior to chemically-treated surfaces, which in general have poor lubricating properties and lose some dimension as running-in goes on.[2] An additional claim for the tinned piston ring is that replacement rings have a good sales appearance and are protected against rust during storage,[4] a matter felt to have some weight by a firm producing seventy-five million tinned rings annually.

Frettage corrosion associated with slight repeated slip between metal surfaces in close contact can be prevented in some instances by the application of a tin coating to one of the surfaces.[9] The function of the tin is thought to be the making good of deficiencies in the fit between the surfaces.

Success has been obtained with the interface between steel bearing housings and bearing backs, using coatings 0·5–1 mil. thick, and in splined shafts.

Electrodeposited tin coatings are used as a 'stopping off' agent in the nitriding of steel. A coating thickness of 0·2 mil. is adequate, and a coating of 0·2–0·5 mil. is normally applied. Deposits thicker than 0·5 mil. are undesirable since tin, which melts well below the nitriding temperature, may then run off and cover or bespatter surfaces required to be clean.[5]

The high hydrogen overpotential of tin is used in the Bullard-Dunn process of electrolytic pickling for steel.[6 7 8] A dilute sulphuric acid bath containing a trace of tin is used and the work is made the cathode. The anode is of silicon iron with a sufficient area of tin to maintain the tin concentration. Tin plates out on areas of steel as they become scale-free, checking any etching action and evolution of hydrogen, so that the action of the bath is concentrated on the as yet uncleaned surfaces. The merits of the method are thus to provide a pickled surface which is not etched, and which is protected by the tin deposit against rusting on removal from the pickle, and to secure economy in operation, by concentrating action only on those parts of the steel still carrying scale.

The tin coating can be removed if not required but it may usually with advantage be retained to provide protection in storage or a convenient surface for subsequent hot-tinning, white annealing or painting.

REFERENCES

1. Glasson, G. W., Month. Rev. Am. Electroplaters' Soc. (1932) **19**, 10.
2. Lewis, W. R., Tin and Its Uses (1940) No. 7, 12.
2. Smith, D. M., Trans. Soc. Auto. Eng. (1945) **53**, 521.
3. Yates, B. A., S.A.E. Journal (1939) **44**, 49.
4. Lane, P. S., quoted in Tin and Its Uses (1949) No. 21, 6.
5. Struyck, C., Month. Rev. Am. Electroplaters' Soc. (1946) **33**, 394.
6. Fink, C. G. and Wilber, T. H., Trans. Electrochem. Soc. (1934) **66**, 381.
7. Kronsbein, J., J. Electrodep. Tech. Soc. (1940) **16**, 55.
8. U.S. Patents 1, 898, 765 and 1,917,022.
9. Wright, O., J. Electrodep. Tech. Soc. (1949) **25**, 51.

CHOICE OF COATING WEIGHT ON TINNED STEEL

The natural tendency is to use the thinnest coating which will, in normal conditions, perform the task required, and this, originally an effect of price, has been accentuated by tin conservation measures of war or near-war conditions.

In manufacture and handling of food either in industry or in the home, where equipment may be used over and over again, the coating must be thick enough to withstand repeated washing. It is also usually desirable that it should be free of pores, to prevent contamination of the product, although some cooking utensils, such as baking tins, soon have their pores filled with grease.

In canning fruit, there must be sufficient tin present to protect exposed steel for a substantial storage period. The thinner coatings commonly produced on electrolytic tinplate lines have, without lacquer protection, an inadequate storage life. A comparison of life of an electrolytic tinplate with that of hot-dipped tinplate gave the results shown in Table X.[1] The electrolytic plate had 0·5 lb. per basis box and the hot-dipped plate 1·25 lb. per basis box and neither was lacquered.

TABLE X

EFFECT OF COATING WEIGHT ON STORAGE LIFE

Product	*Coating*	*Days of storage at 38° C.*	*Vacuum loss (in.)*	*Failures per 1,000 cans*
Grapefruit ..	Hot-dip	159	0·2	0
	Electro	159	6·0	0
Tomato Juice ..	Hot-dip	225	0·2	0
	Electro	225	9·1	216

Lacquering the electrolytic plate enables it to be used successfully for the less corrosive packs, but even with special stripe lacquering of the seam, the performance is not entirely satisfactory for the more corrosive materials.

The need for porosity control in the inside of fruit cans, as distinct from weight of tin present, has been questioned. It has been shown, for prunes at least, that a tin layer, with gross discontinuities may be as effective, if there be enough tin there, as a normal coating,[2] but it seems likely that in general the exposure of a greater area of steel must increase the number of active hydrogen-evolving points exposed. Moreover, the restriction of porosity is very desirable in order that external rusting in storage may be minimised.

Containers for petrol and oil, liable to receive adventitious water, should be as free from pores as possible in order to reduce the chance of water drops alighting on exposed steel. Dry goods on the other hand may be kept in containers with light-weight porous coatings for long periods without causing any disfigurement although, even with these, the risk of marring by rust of the outside of containers rises with increase in porosity of the coatings. Moreover the internal surface above some products that have themselves no direct effect

on tinplate may be rust-marked by their vapours or, if they are only gradually consumed, by vapours gaining access from external sources after the container is opened. In instances where such an effect would be specially disadvantageous by reason of appearance of the container or discoloration of the product, the use of a superior grade of tin-plate, or its improvement by lacquer or chemical treatment may be justified.

TABLE XI

RECOMMENDED THICKNESSES OF ELECTRODEPOSITED TIN COATINGS

Purpose	*Coatings on Iron and Steel*	
	Minimum total thickness (inches)	*Average thickness (inches)*
Corrosion and Abrasion (especially for use in food handling)	0·002	0·003
Indoor Atmospheric Corrosion (not painted or otherwise protected) and less severe forms of wet corrosion	0·0008	0·001
Screws and Threaded articles . .		0·0002
To facilitate soldering	0·0002	0·0003
As a preparation for protective painting	0·00003	0·00005
As a stop-off in nitriding	0·0002	Not more than 0·0005

These considerations lead to a rough allocation of the thickness of coating required for various purposes somewhat as follows.

For food processing equipment, possibly subject to some abrasion and to frequent cleaning, and required to expose no corrodible metal to the product, coatings may be over 3 mil. thick. Such coatings are applied by spraying or electrodeposition. Normally the conditions are not so exacting and the common run of hot-dipped coatings of 0·5–1 mil. thick is adequate for much service with food and dairy products.

Some dairy and kitchen equipment may satisfactorily be produced from the better grades of tinplate with a coating of 0·1–0·2 mil (1·75–3·5 lb. basic box). Other services which require this grade of coating with its low porosity

are petrol tanks, gas meters and electrical apparatus likely to be exposed to corrosive conditions.

The canning of fruit is carried out with tin-plate carrying coatings of 0·06–0·11 mil. (1·0–1·75 lb. basis box), the largest amounts being taken from the lower end of this range and the better quality plate reserved for the more demanding packs.

For containers of paint and other non-corrosive materials, including dry goods and for decorated boxes, screw caps, closures, toys, etc., which are required to maintain a good appearance in mildly corrosive environments, coatings of 0·03–0·08 mil. (0·5–1·25 lb./basis box) suffice. Even lighter coatings, produced by the electrolytic tinning lines, are used, plain, for dry packs for good or short storage conditions and, lacquered, for a very large range of materials.

A British Standard Specification is being prepared to indicate the thickness of electrodeposited tin required for various purposes. Some interim suggestions are shown in Table XI.

REFERENCES

1. Brighton, K. W., Trans. Electrochem. Soc. (1943) **84**, 227.
2. Vaurio, V. W., Corrosion (1950) **6**, 260.

TESTS FOR TIN COATINGS ON STEEL

The most important qualities of the tin coating are its thickness and porosity. The methods of measuring thickness have been conveniently summarised in another publication.[1] The most generally useful method is to dissolve the tin from a weighed sample in concentrated hydrochloric acid in which 20 g/l of antimony trioxide have been dissolved.[2] This method removes the tin-iron alloy layer as well as tin and, where precision is required, a correction may be applied.

A method specially applicable to rapid routine determinations is to dissolve the tin anodically in hydrochloric acid containing iodine. The excess iodine is titrated when solution is complete.[3] This method determines the tin only and no correction for alloy layer is required. Other methods of electrolytic stripping are also employed.

For assessing porosity, there are three principal methods. Absorbent paper wetted with a solution of sodium chloride and potassium ferricyanide may be applied to the cleaned surface. The number of blue spots developed is counted or compared with standard papers.[4] Alternatively, the carefully cleaned metal may be immersed in distilled water at 95° C. for about six hours and the rust spots counted or compared with standards.[5] This method, although very good when properly applied, calls for rather critical control. The distilled water

must have pH value 3·5–5 and be free of copper. The application of the test to thin coatings is made easier by pre-immersion in 10 per cent. chromic acid at 90° C. This has the effect of making the rust spots less diffuse.[6]

Probably the best method, although it gives no indication of the distribution of the pores, is the Thiocyanate Test.[6] In this the cleaned sample, with edges protected by wax, is placed in a solution of ammonium thiocyanate, acetic acid and hydrogen peroxide for 15 minutes. The iron dissolved and converted to ferric thiocyanate is then estimated colorimetrically. Some difficulty has been experienced in obtaining results reproducible in different laboratories, but careful control promises to overcome this.[7]

In view of the importance of the nature of the *steel base* of tinplate in canning, attempts have been made to assess its suitability by laboratory tests. A method of measuring the rate of hydrogen evolution in N. hydrochloric acid[8] has given some promise, but in view of the apparently different requirements of various packs, it seems unlikely that any one simple test will be universally applicable. The development of short time tests suited to particular groups of products may however be expected. For instance, for a large number of steels, a good correlation was obtained between rate of corrosion of the bare steel in boiling 11 per cent. hydrochloric acid and the incidence of hydrogen swells in cans formed from the tinned and lacquered sheet and packed with either raspberries, strawberries or czar plums.[9] It is interesting that correlation between failures in the canned products and the rate of corrosion in cold fruit juice or citric acid open to the air was not good. The basis of test must clearly involve corrosion of predominantly the hydrogen evolution type.

REFERENCES

1. Price, J. W. and Hoare, W. E., Determining the Thickness of Tin Coatings, Tin Res. Inst. Pub. TTE, 1949.
2. Clarke, S. G., Analyst (1934) **59**, 525; Trans. Electrochem. Soc. (1936) **69**, 131.
3. Bendix, G. H., Stammer, W. C., and Carle, A. H., Ind. Eng. Chem. (Anal.) (1943), **15**, 501.
4. Pitschner, K., T.A.S.T.M. (1927), **27**, 304.
5. Macnaughtan, D. J., Clarke, S. G. and Prytherch, J. C., J. Iron and Steel Inst. (1932) **125**, 159.
6. Kerr, R., J. Soc. Chem. Ind. (1942) **61**, 181.
7. Pearson, J. and Bullough, B. W., J. Iron and Steel Inst. (1948) **160**, 376. (See also discussion by Hoare, W. E. and Caulfield, K. W., ibid. (1949) **163**, 17.)
8. Vaurio, V. W., Clark, B. S. and Lueck, R. H., Ind. Eng. Chem. (Anal.) (1938) **10**, 368.
9. Hoar, T. P., Morris, T. N. and Adam, W. B., J. Iron and Steel Inst. (1941) **144**, 133P.

TIN COATINGS ON COPPER AND COPPER ALLOYS

Copper and its alloys are tinned by immersion in molten tin, by electrodeposition, by spraying, by wiping or by chemical replacement. In hot-dipping, it is necessary to limit the immersion time as there is a considerable alloying action and the tin bath may become fouled by copper-tin alloy; otherwise the methods are similar to those used for steel.

Copper itself is usually resistant to corrosion, but small amounts passing into solution have undesired effects on many products. The function of tin coatings is usually to provide, between copper and material handled, a separating layer which, if it is corroded at all, will yield an innocuous corrosion product. It is therefore very desirable that the tin layer shall be as complete as possible. Much attention has been fruitfully given to methods of hot-tinning which will keep porosity to a minimum. These, with the methods of determining the thickness and continuity of the coatings, have been conveniently summarised in another publication.[5]

Tin coatings on copper and brass may also be produced by exposure to volatilised stannous chloride in a hydrogen atmosphere,[6] a process known as 'stannising'. The coating consists of an alloy of tin and the basis metal having a structure influenced by the time and temperature of deposition. The value of this method is that even coatings can be obtained over irregular surfaces, and it has only special applications where this virtue is particularly useful.

Chemical replacement methods of tinning have been used mostly to produce thin coatings for light duties, but means are available of obtaining coatings of high performance. One method found suitable for coating tubes is to immerse the work in a solution of stannous chloride, caustic soda and sodium cyanide.[3] The method of connecting the work to aluminium in sodium stannate solution, mentioned for steel (p. 45) is also applicable to copper.

Tin is usually anodic to copper, but it is possible for a tin coating, after a period of use in some water supplies that produce on it a special form of surface film, to cease to give protection to copper exposed at its discontinuities and even to become cathodic to it.[2] [8] This development is said to be favoured by high contents of carbon dioxide, oxygen and calcium salts in the water and by increase in temperature.[8] It has probably been responsible for some failures in tinned copper pipes, but the general experience is that tin-coating is a useful protection against pick-up of copper by cold soft waters and also in vessels such as urns, kettles and wash-boilers used for hot water. It also protects refrigerator parts exposed to repeated condensation of water. Any complaints that arise from these uses refer normally not to attack of the copper but to disfigurement of the tin coating.

This marking of the coating takes the form of small dark spots that gradually increase in size. The rate of penetration of the coating is slow and the action is usually only noticed in conditions which leave the surface quite unobscured by scale from the water. It seems to be an instance of the 'black spot' formation such as may be experienced on pure tin in some water supplies (p. 23). For tin coatings on copper however the surface defects which can promote the

action on solid tin may be augmented by others associated with the coating process.

Pores in the coating and the inclusion of fragments of tin-copper compounds in the surface layers may be expected to stimulate corrosion of the coating surrounding them. The tin-copper alloys are cathodic to tin and the copper-rich ones may even be slightly cathodic to copper.[1] They are formed during coating by hot-dipping and by wiping and may be developed in time in electrodeposited coatings by diffusion. In well conducted hot-dipping and in electrodeposition the alloys should not appear in the surface of the coating, but, in wiping, especially if there is overheating, a greater chance of this occurrence appears possible. An additional possibility arising with wiped coatings is the stimulation of local corrosion by residues of flux. These should be carefully removed as recommended for soldering (p. 34).

In the dairy and food industries where tinned copper finds its greatest applications, there appears to be little protection of the copper at breaks in the coating, although the corrosion of either tin or copper is usually very slight. Copper foil tinned by electrodeposition and immersed in fresh or sour milk contributed similar very small amounts of copper to the milk, whether the coating was 0·02, 0·04 or 0·06 mil. thick, Coatings produced by rolling down tinned copper strip, even when 0·12 mil thick, allowed rather more copper to pass into the milk, apparently because this procedure increased the area of copper exposed at discontinuities in the coating.[7] In practical dairy work, the exposure of copper by the gradual loss of the tin coating, is thought to result quickly in taints associated with copper in milk. The most important matter therefore is to ensure that tin coating is complete and is well preserved. The relevant questions of corrosion of tin by aqueous solutions, milk and cleaning agents have already been dealt with (pp. 22, 25 and 26).

TABLE XII

THICKNESS OF ELECTRODEPOSITED TIN COATINGS REQUIRED ON NON-FERROUS METALS

Purpose	*Minimum local Thickness (inch.)*	*Average thickness (inch.)*
Corrosion and Abrasion (especially for use in food handling)	0·0015	0·002
Atmospheric Corrosion	0·0003	0·0005
Screws and Threaded articles . .		0·0002
To facilitate soldering	0·0003	0·0005

The tinning of copper wire prior to the application of rubber insulation serves three purposes, providing easy solderability, protecting the copper against tarnishing by sulphur in the rubber insulation and preserving the rubber from ageing changes accelerated by copper. A coating of low porosity is needed for good performance and special tests to check the quality have been devised.[5] Copper wire for fuses is tinned in order to prevent the formation of layers of corrosion product which may obstruct the breaking of the wire when it is molten.

Tinning of brass condenser tubes has been practised with apparent benefit in sea-water, but in fresh water, the merits seem doubtful.[4] The use of tubes of more resistant alloys seems generally to be preferable.

Tin coatings are applied to small brass articles such as pins by immersion in special solutions without applied current, e.g. the articles are immersed with tin in a hot solution of potassium hydrogen tartrate and sodium chloride. Such articles are not normally exposed to severe corrosive conditions and the thin tin coating suffices to maintain a bright appearance.

The choice of coating weight for electrodeposited tin coatings on non-ferrous metals for various purposes is being made the subject of a British Standard Specification. Some interim suggestions are shown in Table XII.

REFERENCES

1. Bauer, O., Vollenbruck, O. and Schikorr, G., Mitt Mat. Pruf. Anstalt. (1932), Sonderheft **19**, 3.
2. Dufton, A. and Brady, F. L., Nature (1927) **120**, 367.
3. Sullivan, J. D. and Pavlish, A. E., Metals and Alloys (1940) **11**, 131.
4. Evans, U. R., Metallic Corrosion Passivity and Protection, 2nd Ed. (1946), Ed. Arnold and Co. Ltd., London, p. 380.
5. Hoare, W. E., Hot Tinning, Tin Res. Inst. Pub. TOI (1948).
6. Gonser, B. W. and Slowter, E. E., Tin Res. Inst. Pub. No. 76 (1938).
7. Kerr, R., J. Soc. Chem. Ind. (1942) **61**, 128.
8. Haase, L. W., Gesundheits Ing. (1933) **56**, 593.

TIN COATINGS ON LEAD

Coatings may be applied to the interior of lead pipe, to protect it from plumbo-solvent water, by electrodeposition, by running molten tin through the pipe or by extruding the two metals together. Tests[2] in a variety of water-supplies indicated that very little tin was removed from tinned lead-pipe, but it appears that, in order to achieve the object of minimising lead take-up, the deposit should be of low porosity.[4] The extrusion process seems likely to achieve the best result in this respect.

A method of testing the porosity of the electrodeposits has been developed[1] in which the test-piece is made the anode in a solution containing potassium

chromate and sodium acetate. The pores become marked as brown spots of lead peroxide or, under appropriate conditions, the current passed by the anode gives an indication of exposed lead. It was found that porosity was negligible for coatings thicker than 0·0005 inch deposited from a stannate bath.

Tin-coated lead foil and collapsible tubes are used as substitutes for pure tin. Sheets or slabs of lead are first coated with tin and are then rolled down or extruded to produce foil or tubes. The coating is usually extremely thin and may contain discontinuities as patches which cover an area much greater than the metal exposed at pores in an electrodeposited coating. Such patches receive little or no protection from the tin coating so that tinned lead foil or tubes may not be well suited to conditions unfavourable to the use of lead, although they always retain a better appearance and, with the possible exception of some acid products,[5] contribute less lead to material in contact with them than would the uncoated metal.

The take-up of lead by whole milk from lead foil was restrained by tin coatings, upwards of 0·075 mil. thick, sufficiently to consider that no harmful contamination resulted, but cream removed amounts of lead that could not be tolerated.[3] This difference was attributed to the formation of an insoluble protein compound with lead in the whole milk and to the production of soluble lead compounds with the fatty acids in the cream. This illustrates the general position that lead will be taken up from the tin coated metal by materials corrosive to lead and that great caution is needed in permitting contact with tinned lead, foodstuffs and medicinal products which may be made harmful by lead contamination.

Appearance also may be marred in environments unfavourable to lead. The author has observed capsules of tinned lead to become disfigured by acetic acid vapour or by vapours from wood which were corrosive to lead.

REFERENCES

1. Baier, S. and Hoar, T. P., J. Soc. Chem. Ind. (1939) **58**, 69.
2. Clark, H. W., J. New England Water Works Assoc. (1927) **41**, 31.
3. Kerr, R., J. Soc. Chem. Ind. (1942) **61**, 128.
4. The action of water on lead, with especial reference to the supply of drinking water, Water Pollution Research, D.S.I.R., Tech. Paper No. 4 (1934).
5. Menard, D. F., J. Am. Pharm. Ass. (1943) **32**, 210.

TIN COATINGS ON ALUMINIUM

Although nothing is known of the resistance to straightforward corrosion of tin coatings on aluminium and its alloys such coatings have had one important application: the tinning of pistons for use in internal combustion engines. The

benefits obtained are just those which were described for the tinning of cast iron pistons (p. 58), i.e. resistance to scoring and scuffing during the running-in period.

Tinning the pistons without tinning the rings does not eliminate scuffing, but if both pistons and rings are tinned, very satisfactory results are obtained. The wear of tinned pistons was found[1] in test operations of 10,000 miles' running to be only one third of that of untinned parts and to be less than that of pistons treated by alternative methods.

The coatings are formed on immersion in sodium stannate solution by chemical replacement. The cleaning of the surface beforehand and the conditions of immersion need careful control to ensure adherent continuous deposits and the various aluminium alloys require slight modifications in the process in order to obtain the best results. Details may be obtained from the Tin Research Institute.[2]

REFERENCES

1. Yates, B. A., S.A.E. Journal (1939) **44**, 49.
2. Hoare, W. E., Immersion Tinning of Aluminium, Tin. Res. Inst. Memorandum OF 225 (1945).

TIN-LEAD ALLOY COATINGS

Coatings of tin-lead alloy may be produced on steel or on copper and its alloys by hot-dipping, electrodeposition or wiping. The most widely used method is hot-dipping for which the procedure followed resembles that used in the production of tin coatings.

The hot-dipping process can be used to produce coatings with tin contents of 2 per cent. upwards and compositions may be chosen to suit particular requirements. Steel sheets are coated in a manner analogous to the production of tinplate to yield terne-plate. There are three standard British grades of this product:[1] tin terne, with 25 per cent. of tin; Special A, with 15 per cent. of tin and terne, with 2 to 10 per cent. of tin. American grading[9] is rather different, the normal grades of terne-plate, including 'roofing tin', being required to have 20 to 25 per cent. of tin in the coating. In both countries the coatings with less than 5 per cent. of tin are commonly regarded as lead coatings. Considerations of cost and conservation of tin tend to change the composition in general use. In Great Britain, the most largely used composition is probably now about 10 per cent. of tin.

The coating thicknesses applied to terne-plate vary from about 0·016 to 0·8 mil. (They are often quoted as lbs. per double basis box, i.e. the area taken is twice that used for tinplate (p. 45) and 1 lb. per double basis box represents a coating thickness of 0·02 mil. on common terne plate). The coating thickness on other material varies with the service required, in the same range.

Tin-lead coatings have for some purposes the advantage over tin coatings of:

1. Lower cost.
2. In coating copper, the lower temperature necessary in hot-dipping produces less alloying and thus reduces contamination of the bath.
3. A better resistance to atmospheres heavily polluted with oxides of sulphur.
4. The coating facilitates deep drawing and stamping of steel.

The disadvantages are: inferior appearance, unsuitability for contact with foodstuffs, and liability to corrosion by materials which affect lead, such as unseasoned wood. (An instance is known where the substitution of terne-plate for tinplate in lining wooden cases led to trouble).

Terne-plate is used for containers of materials such as paint where appearance is not of great importance, for petrol tanks of motor vehicles, and for roofing sheets and light structures, more especially when an acid industrial atmosphere has to be countered. The coating is cathodic to steel and is preferably painted for applications involving exposure to the weather, but its superior paint retention, acid resistance and solderability frequently make it preferable to zinc.

In outdoor exposure tests[2] of unpainted coatings on steel, tin-lead alloys with 2 and 12 per cent. of tin gave good protection in an industrial atmosphere (Sheffield). Here, although fine rust spots appeared, they developed very slowly and the coating itself was only slowly attacked, becoming covered with a white layer of presumed lead sulphate. Coatings 0·6 mil. thick had not reached the grade of 5 per cent. of the surface rusting, considered as failure, after five years, but zinc coatings up to 2·8 mil. thick had failed. In rural and marine environments the lead-tin coatings allowed a much more rapid spread of rust and the failure grade was reached in about a year, whereas zinc coatings performed extremely well.

The cathodic relation to steel of the coatings makes them sometimes unsuitable for use immersed in aqueous solutions, especially those of high electrical conductivity. Nevertheless they do find some employment in vessels for agricultural use and in relatively feeble corrosive solutions. Automobile radiators of steel, assembled and coated at the same time by dipping in a solder bath give good service although not so reliably as those made from copper and similarly treated. The steel bodies of acid-soda type fire-extinguishers are also coated with lead-tin alloy. As a safeguard in this application against any corrosion that might be induced by unsuitable water used in making up the bicarbonate solution contained in the device, the addition of 1 oz. trisodium phosphate to each gallon of the solution has been recommended.[3] Inhibitors or coatings of lacquer or wax[11] may also be used as for tinplate containers (p. 54) when metallic contamination of products such as varnish has specially to be avoided.

Hot-dipped coatings containing 20 per cent. of tin and 80 per cent. of lead are used as stopping-off agents in the nitriding of steel[4] as a less costly alternative to tin.

Tin/lead coatings are applied by hot-dipping to copper parts, such as heat exchangers and combustion chambers, which are exposed in the flues of water-heaters and other gas-heated appliances. An 80 lead—20 tin alloy is commonly used, giving the resistance to the action of the products of combustion, which is necessary to preserve the life of the installation and, also to prevent blockage of the flue by corrosion product. Some corrosion does occur and the coating is in time destroyed, but in comparative tests[5] of a large number of materials, coatings of tin-lead (66 per cent. tin) or tin on copper were the most resistant to burnt coal gas. Experiments[6] with the 20 per cent. tin alloy showed that the corrosion varies with the temperature of the flue gas, reaching peak values at the dew point of the gases and at about the temperature which would be the dew point in the absence of sulphur trioxide from the gas. Corrosion declined gradually above the dew point to reach steady values for temperatures more than 20° above it.

Wiped coatings may be usefully employed when hot-dipping or electrodeposition is not possible. They may conveniently be used to provide local protection to vulnerable areas, e.g. instead of tin, to give additional protection to the edges of work that is to be painted (p. 59).

Electrodeposited tin-lead coatings now attract interest chiefly as a preparation for soldering and as an overlay for bearings, but they have a good corrosion resistance. The development of the process of deposition from a fluoborate bath and the use as a solderable deposit have been reviewed elsewhere.[7]

In some tests[8] of alloys with up to 15 per cent. tin, a deposit with 5·5 per cent. tin seemed rather better than alloys of higher tin content or than lead coatings either in salt spray or out-of-doors exposure. Rust occurred at pores, however, and since the coating is not decorative, it will probably find special rather than general application. One such application was the coating of the inside of poison gas containers in the first World War:[10] others will no doubt be for those services found suited to hot-dipped tin-lead coatings, but involving articles which cannot be hot-dipped.

REFERENCES

1. British Standards for Steel and Steel Products, Handbook No. 10 of the British Standards Institution (1949), p. 73.
2. Hudson, J. C. and Banfield, T. A., J. Iron and Steel Inst. (1946) **154**, 229P.
3. Hewlett, W. L., Chem. and Ind. (1935) **54**, 1094.
4. Tin and Its Uses, No. 8 (1941), p. 8.
5. Taylor, F. and Wood, J. W., Trans. Inst. Gas Eng. (1939-40) **89**, 339.
6. Kerr, R. and Withers, S. M., J. Inst. Fuel (1949) **22**, 204.
7. Cuthbertson, J. W., J. Electrod. Tech. Soc. (1950) **26**, 99.
8. Du Rose, A. H., Trans. Electrochem. Soc. (1946) **89**, 101.
9. Soderberg, G., The Corrosion Handbook, Ed. Uhlig, H.H. (1948) J. Wiley and Sons Inc., New York, p. 856.
10. Hiers, G. O., Ibid., p. 216.
11. Bruins, P. F. and Gardner, W. H., Ind. Eng. Chem. (1939) **31**, 1178.

TIN-ZINC ALLOY COATINGS

Tin and zinc can be co-deposited in all proportion from a solution containing sodium stannate, sodium hydroxide, sodium zinc cyanide and free sodium cyanide.[1 2] The composition of the deposit is adjusted by varying the concentrations of zinc, total cyanide and sodium hydroxide, but the operating difficulties increase as the conditions are adjusted to deposit less than 50 per cent. American development[4] has favoured the substitution of potassium salts for the sodium salts of the original solution, in order to secure higher rates of deposition.

Corrosion tests, in humidity chamber and in salt spray of deposits on steel with zinc contents between 8 and 72 per cent. gave a good indication of the most favourable composition range.[3] Coatings with a zinc content of less than 14 per cent. permitted rusting at pores with little corrosion of the coating itself, in a tin-like manner. Coatings with more than 30 per cent. of zinc were more zinc-like, the coating being corroded, but protecting the steel until it was substantially removed. Coatings with a composition around 80 per cent. tin, 20 per cent. zinc seemed to offer a good compromise, pore-rusting being checked but the coating being only slowly attacked.

Deposits of this composition gave protection against rusting for longer than zinc deposits of similar thickness in salt spray. Good protection was provided on complicated shapes owing to the excellent throwing power of the bath, and the capability of plated sheet to stand deformation without serious deterioration in protective value was demonstrated.

Further experience has confirmed that a deposit with 20–30 per cent. of zinc is the most generally satisfactory. Such a coating plates smooth, although not bright, to give a pleasant appearance, and is very solderable. The appearance can readily be brought to a decorative standard by scratch-brushing or polishing and is retained sufficiently well to permit the use of the coating as a clean-looking finish on many articles in domestic and industrial use.

Electrode potential measurements made with thick deposits give values similar to those obtained with zinc,[2] but protection of steel exposed at pores in the deposit is not as reliable as it is with zinc coatings. Much of the protection against rusting probably depends on the fineness and fewness of the pores. The deposit is extremely fine-grained and a sufficient thickness readily gives complete protection against pore rusting. A minimum thickness of 0·3 mil. is required for this and a thickness of 0·5 mil. can be generally recommended for safety.

Resistance to finger-marking and to staining by condensation and some restraint on rusting at breaks in the coating can be obtained by a passivating treatment. One much used method is to immerse the work after plating and rinsing in 2 per cent. chromic acid solution at a temperature of 50–80° C. The time of treatment required diminishes as the temperature is raised, varying from 15 secs. at 50° C. to 5 secs. at 80° C. Higher temperatures and longer immersion periods tend to give rather better protection but may produce some discoloration of the deposit. Another good method which has the ad-

vantage of operation at room temperature is immersion in a solution of 1 per cent. sodium dichromate and 0·033 per cent. (by weight) of sulphuric acid for ten secs. This process may produce slight discoloration of the deposit but provides excellent protection.

In full exposure to the weather, the alloy coating will not normally prevent rust for as long as zinc coating of the same thickness,[6] but its good performance in environments involving moisture condensation, especially the relative freedom from formation of bulky corrosion products, and its excellent solderability make it preferred for many purposes. Its competitor as an easily solderable coating, cadmium, can only equal its protection to steel in purely marine conditions and is much inferior in industrial atmospheres.[6] Tin-zinc is therefore tending to displace cadmium from its place as a solderable protective finish in the electrical and radio industries, a process assisted by the lower cost and, in recent times, the greater availability of the alloy.

Like zinc and cadmium, tin-zinc is apt to form a white corrosion product when exposed to the acid organic vapours which are evolved from some insulating materials such as yellow Empire tape, but can be protected by the passivating treatment mentioned above.

Experience in commercial application for electrical and radio work has been reviewed[5] with the conclusion that, at the prices ruling in 1948, there was an appreciable saving in cost by the substitution of the alloy for cadmium. Other commercial uses of the coating include motor-cycle components, typewriter parts, tools and skates: many extensions are anticipated. One promising development is that the coating appears to be a suitable one for application to ferrous nuts and bolts and other components used in contact with aluminium, as a means of giving protection to them without stimulating galvanic corrosion.

Although the tin-zinc alloy coating is now considered to be one containing 20–30 per cent. tin, some use is made of smaller additions of tin to zinc coatings, applied either by electro-deposition or by hot-dipping, mainly to improve appearance.

The addition of 1–2 per cent. of tin to zinc cyanide plating baths in order to brighten the deposit has been practised, but the corrosion resistance is believed to be unaffected.

Addition of about 1 per cent. of tin to hot-dip galvanising pots improves the appearance of the coating, producing a smooth white coating with a well-defined spangle.[7] The flexibility of the coating was found to be somewhat reduced, although this effect was slight if immersion time in the molten metal did not exceed one minute. With tin additions greater than 1 per cent. a yellowish tarnish tended to develop as the coatings cooled. It has been suggested[8] that large tin additions promote the formation of 'white rust' on galvanised coatings in storage but the general indications are that the small additions commonly used are without effect on corrosion resistance.

The combined addition of aluminium and tin to hot-dipped zinc coatings was explored with the conclusion that coatings of bright lustrous appearance with good flexibility could be obtained with a zinc bath containing 0·02–0·03

per cent. aluminium and 0·5 per cent. tin with dipping times of less than two minutes.[7]

The attack on the steel base during immersion for one hour at 450° C. in mixtures of tin and zinc in the range 0–100 per cent. tin was little affected for mixtures with less than 50 per cent. of tin.[9] For greater percentages of tin the attack was reduced. Coatings with 50 per cent. tin, 50 per cent. zinc have been produced by hot-dipping at the Tin Research Institute. The greater fluidity of the bath as compared with zinc enabled smooth, relatively thin coatings to be produced. The corrosion resistance appears to be similar to that of the electrodeposited alloy coatings, but drossing losses in the hot-dipping process were high and there has been no commercial application for it.

REFERENCES

1. Angles, R. M., J. Electrodep. Tech. Soc. (1946) **21**, 45.
2. Cuthbertson, J. W. and Angles, R. M., J. Electrochem Soc. (1948) **94**, 73.
3. Angles, R. M. and Kerr, R., Engineering (1946) **161**, 289.
4. Lowenheim, F. A. and MacIntosh, R. M., J. Electrodep. Tech Soc. (1951) **27**.
5. Miller, P. J. and Cuthbertson, J. W., Metal Finishing (1949) **47**, 44.
6. Britton, S. C. and Angles, R. M., Metallurgia (1951) **44**, 185.
7. Hall, W. L. and Kenworthy, L., Sheet Metal Ind. (1947) **24**, 741.
8. Imhoff, W. G., Iron Age (1932) **129**, 232.
9. Bablik, H., Galvanising (Hot-dip) 3rd Edition, 1950. E. and F.N. Spon Ltd., p. 225.

TIN-CADMIUM ALLOY COATINGS

Alloy coatings containing tin and cadmium in various proportions have been successfully deposited from an acid sulphate bath.[1] The corrosion resistance of such coatings changed from tin-like to cadmium-like as the composition was varied and no special property has yet emerged which would justify the complications required for the deposition to make the alloy preferable to one or other of the constituent metals or to tin-zinc alloy.

Claims have been made however for good resistance to salt spray of deposits produced either by diffusing together cadmium (0·05 mil.) plated over tin (0·05 mil.), by heating at 170° C. for thirty minutes, or by electrodeposition of an alloy with 75 per cent. cadmium, 25 per cent. tin from a fluoborate bath.[2] A considerable improvement over both tin and cadmium in resistance to salt spray was reported for the deposits and rather surprisingly, protection at a scratch through the deposit was obtained. If these results are confirmed there will, no doubt, be many commercial applications for such coatings. Good results have already been obtained on aircraft parts subject to corrosion in

addition to galling or alternating stress, e.g. compressor housings and the exposed part of the propeller shaft.[4]

Tin plated over cadmium has been found to give protection against the disfigurement produced by organic vapours such as those given off by some electrical insulating materials.[3]

REFERENCES

1. Bennett, P. S., J. Electrodep. Tech. Soc. (1950) **26**, 91.
2. Scott, B. E. and Gray, R. D., Iron Age (1951) **167**, 59.
3. Seabright, L. H. and Trezek, J., Plating (1948), 715.
4. Promisel, N. E. and Mustin, G. S., Corrosion (1951) 7, 379.

TIN-COPPER ALLOY COATINGS

The ancient use of tin-copper alloys to produce tarnish resistant mirror surfaces has already been mentioned (p. 39). Such alloys can readily be electrodeposited from a mixed cyanide bath to give deposits to which the name speculum or 'white bronze' has been given.[1]

A deposit of 42 per cent. tin, 58 per cent. copper is preferred as giving a good colour and best tarnish resistance. With less than 39 per cent. tin, tarnishing readily occurs: with more than 55 per cent. of tin the deposit is soft. The deposit in the recommended range has been shown by X-ray examination[2] to consist mainly of a cubic phase Cu_3Sn, which is metastable at room temperature, but remains unchanged indefinitely unless heated to 200° C.

The coating as deposited is usually smooth, matte, but is polished readily to a high lustre. Bright deposits can be obtained by adding to the plating bath organic brightening agents either alone or in addition to small amounts of lead,[3] but difficulty is found in consistently obtaining a bright deposit over the surface of an irregularly shaped article.

The coating is noble and will not give protection to the basis metal exposed at pores. Thicknesses adequate to keep porosity very low are therefore desirable. Recommended minimum values are: 0·5 mil. on brass, copper, nickel silver, etc., and 1 mil. on steel.

The tarnish resistance, although very good, is not the equal of that of chromium or of tin-nickel alloys. The deposit becomes dulled on exposure to atmospheres containing appreciable amounts of sulphur dioxide, although it resists hydrogen sulphide well. It cannot generally be recommended for use out of doors as it becomes dull grey in time if not frequently cleaned. The coating is, however, very useful for decoration of metalware used indoors. For such a purpose its silver-like colour is very suitable, being more pleasing than that of chromium. It resists the action of most foodstuffs and is suitable for cutlery. The high specular reflectivity of the polished deposit, 70 per cent. as

against 90 per cent. for silver and 61 per cent. for chromium for untarnished material, and superior to silver after a short period in mildly tarnishing conditions,[4] makes the alloy very suitable for reflecting purposes. Commercial uses include cutlery, reflectors, oil-lamps, electric irons, vacuum cleaners and decorative hollow-ware.

Bronzes of a range of composition have been electrodeposited[5 6 7] and many deposits had found some use as decorative coatings before the special virtue of the speculum composition was established. Compositions outside the speculum range are not resistant to tarnish, but have the normal corrosion resistance of bronzes and may therefore be suited to special applications. One such is the use of deposits with 10–20 per cent. tin as stop-off coatings in nitriding.[8] Superiority over tin is claimed for this purpose, as the alloy is harder and therefore resists damage in handling better, and as its higher melting point avoids flow of the deposit which can be troublesome with tin during the nitriding process.

REFERENCES

1. Angles, R. M., Jones, F. V., Price, J. W. and Cuthbertson, J. W., J. Electrodep. Tech. Soc. (1946) **21**, 19.
2. Rooksby, H. P., J. Electrodep. Tech. Soc. (1950) **26**, 119.
3. Bennett, P. S., J. Electrodep. Tech. Soc. (1950) **26**, 107.
4. Tin and Its Uses (1940) No. 4, 4.
5. Bechard, C., J. Electrodep. Tech. Soc. (1936) **11**, 15.
6. Baier, S. and Macnaughtan, D. J., J. Electrodep. Tech. Soc. (1936) **11**, 1.
7. City Auto Stamping Co., U.S. Patents No. 1,970,548 and 1,970,549; British Patents No. 409,001, 412,277 and 425,846.
8. Struyk, C., Month. Rev. Am. Electroplaters Soc. (1946) **33**, 394.

TIN-NICKEL ALLOY COATINGS

Deposits of tin-nickel alloy, plated from a mixed cyanide-stannate bath, were found to be hard, uncorroded by nitric acid and with nickel contents of 18–25 per cent., bright as deposited.[4] These deposits have had no practical application, as the rate of deposition was low.

Alloy coatings produced on steel by depositing tin on top of an equal thickness of nickel and then heating were shown to have good corrosion resistance to some fruits and vegetables under anaerobic conditions and to be anodic to steel in these conditions.[5] The complication of two electrodeposition processes and a heat treatment weighs heavily against the wide application of this process.

Recently the future of tin-nickel alloy coatings has been made immensely more promising by the discovery that alloys can be deposited bright at a satis-

factory rate from an acid fluoride bath containing salts of both metals.[1] A deposit containing 65 per cent. tin, a composition found very easy to maintain, has a pleasant colour, is hard (600-700 Vickers Pyramid Number) and has very high resistance to tarnishing and corrosion. As for electrodeposited speculum, the coating is shown by X-ray examination[3] to be an intermetallic compound that is metastable at ordinary temperatures. The composition corresponds roughly to NiSn, but the cell structure is a slightly modified form of the hexagonal structure taken by Ni_3Sn_2. This structure remains stable unless the alloy is heated to 360° C.

Out-of-doors, in sea-coast or inland atmospheres, the deposit remains bright indefinitely. It is uncorroded by cold nitric acid of all concentrations, by other acid solutions with a pH greater than 1·2, by neutral solutions and by alkalis, and is not discoloured by foodstuffs, by handling or by exposure to atmospheres grossly polluted with sulphur dioxide or hydrogen sulphide.[2] It may by tarnished by prolonged immersion in water, especially hot water, or by exposure to hot steam for some hours, but is unaffected by hot dry air, up to 320° C. at least, or by the normal wetting or exposure to condensation involved in domestic use.

The coating is cathodic to brass and to steel and pore-sites in coatings on these metals may be disfigured by corrosion product in exposure to the atmosphere and pitted in immersed conditions. Experience, so far, suggests that a coating thickness in excess of 0·5 mil., deposited on brass from a well controlled solution, is sufficiently pore-free for decorative coatings used in atmospheric exposures of moderate severity. On steel, in order to restrain pore-rusting while keeping the thickness within the normal commercial range for decorative coatings, an undercoating of about 0·5 mil. of copper is essential for out-of doors service and, on this, the alloy deposit should have a thickness of at least 0·5 mil. Experience of commercial application is needed before a final assessment is made of the thicknesses that should be specified to give restraint of pore-rusting equal to that given by the standard grades of chromium-on-nickel coatings. Results available from samples plated in the laboratory suggest that deposits of tin-nickel direct on brass or over copper on steel have rather similar porosities to nickel coatings of similar thickness. The alloy coating has of course an advantage over chromium-on-nickel in that it is tarnish-resisting material all through and is thus free from the troubles associated with the deficiencies of the thin chromium layer.

At the time of writing, commercial exploitation of tin-nickel deposition is only just beginning. The development stages have revealed no insuperable difficulties, the composition of the deposit in particular being easy to maintain. There appears little doubt that this alloy coating will prove to be a noteworthy addition to the contributions of tin to the prevention of corrosion in providing a tarnish-resisting decorative coating and, using thick deposits, a corrosion resistant material for use in the food and chemical industries.

REFERENCES

1. Parkinson, N., J. Electrodep. Tech. Soc. (1951) **27**.

2. Parkinson, N., Britton, S. C. and Angles, R. M., Sheet Metal Industries (1951) **28**, 757.
3. Rooksby, H. P., J. Electrodep. Tech. Soc. (1951) **27**.
4. Monk, R. G. and Ellingham, J. H. T., Trans. Faraday Soc. (1935) **31**, 1460.
5. Copson, H. R. and Wesley, W. A., Trans. Electrochem. Soc. (1943) **84**, 241.

Index

Index

Index

Index

[illegible]
3X
7/10/13

‘TIN AND ITS USES’

This illustrated Review will enable you to keep in touch with research and development of Tin; it is issued free by the Institute.

If you would like to be on the mailing list for *Tin and Its Uses* please send a postcard to one of the addresses on the inside front cover.

THE CORROSION RESISTANCE OF TIN AND TIN ALLOYS

S. C. BRITTON, M.A.

TIN RESEARCH INSTITUTE

Printed in England